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Crop bioaccumulation and human exposure of perfluoroalkyl acids through multi-media transport from a mega fluorochemical industrial park, China

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ABSTRACT: Significant quantities of perfluoroalkyl acids (PFAAs) are released to the environment from fluorochemical manufacturing processes through wastewater discharge and air emission in China, which may lead to human exposure and health risks through crop bioaccumulation from PFAAs-contaminated soil and irrigation water. This paper systematically studied the distribution and transport of PFAAs in agricultural soil, irrigation water and precipitation, followed by crop bioaccumulation and finally human exposure of PFAAs within a 10 km radius around a mega-fluorochemical industrial park (FIP). Hotspots of contamination by PFAAs were found near the FIP and downstream of the effluent discharge point with the maximum concentrations of 641 ng/g in agricultural soil, 640 ng/g in wheat grain, 509 ng/g in maize grain and 4,862 ng/L in precipitation. As the distance increased from the FIP, PFAAs concentrations in all media showed a sharp initial decrease followed by a moderate decline. Elevated PFAA concentrations in soil and grains were still present within a radius of 10 km of the FIP. The soil contamination was associated with the presence of PFAAs in irrigation water and precipitation, and perfluorooctanoic acid (PFOA) was the dominant PFAA component in soil. However, due to bioaccumulation preference, short-chain perfluoroalkyl carboxylic acids (PFCAs), especially perfluorobutanoic acid (PFBA), became the major PFAA contaminants in grains of wheat and maize. The bioaccumulation factors (BAFs) for both grains showed a decrease with increasing chain length of PFAAs (approximately 0.5 log decrease per CF_2 group). Compared to maize grain, wheat grain showed higher BAFs, possibly related to its higher protein content. The PFCA (C4-C8) concentrations (on a $\log_{10}$ basis) in agricultural soil and

grain were found to show a linear positive correlation. Local human exposure of PFOA via the consumption of contaminated grains represents a health risk for local residents, especially for toddlers and children.

KEYWORDS: PFAAs; agricultural soil; precipitation; crop bioaccumulation; human exposure

1. Introduction

Perfluoroalkyl acids (PFAAs) have been widely used in industrial processes and household products, including performance chemicals, lubricants, pesticides, surfactants, and surface protectors, owing to their excellent chemical stability, high surface activity, with water and oil repellence (Giesy and Kannan, 2001; 2002). However, their persistence, bioaccumulation, potential toxicity, and long-range transport make them contaminants of emerging concern (Lescord et al., 2015; Liu et al., 2015; Wang et al., 2015b). As a result of their widespread use and resulting emissions, PFAAs have been detected in numerous environmental compartments, such as air (Taniyasu et al., 2013), water (Wang et al., 2012), soil (Meng et al., 2015), sediment (Yeung et al., 2013), wildlife (Persson et al., 2013), plants (Vestergren et al., 2012) and even human tissues (Kannan et al., 2004). Furthermore, due to their mobility in both surface waters and the atmosphere, these two environmental media have become primary carriers of PFAA transportation with soil considered as one of the major sinks (Yamashita et al., 2008; Kwok et al., 2010; Liu et al., 2015).

Manufacturing and use facilities often lead to pollution hotspots of PFAAs in surrounding environments (Xiao et al., 2012; Xie et al., 2013; Liu et al., 2017). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are two of the most frequently detected PFAAs in the environment (Wang et al., 2015a). The discharge of wastes from a manufacturing facility in Alabama, in the USA, has led to high levels of PFOA (598 ng/L) and PFOS (220 ng/L) in the nearby Tennessee River (Hansen et al., 2002; Newton et al., 2017). Affected by a former manufacturing facility in

84 Minneapolis-St. Paul, in the USA, PFAA levels in soil are still as high as 126 ng/g for
85 PFOA and 28.2 ng/g for PFOS (Xiao et al., 2015). PFAAs have been detected in
86 precipitation in regions associated with PFAA-related industries with reports of 152
87 ng/L in Weifang and 229 ng/L in Tianjin, China (Zhao et al., 2013b; Shan et al., 2015).
88 However, to date, most studies about PFAAs pollution from the manufacturing facilities
89 only focused on one or two media, mainly water body. A systematic research on
90 distribution and transport of PFAAs in multi-meida including water, soil, precipitation
91 and crops around a PFAA-related facility has yet to be carried out.

92 A human health concern may arise from the accumulation of PFAAs in food crops
93 (Zhang et al., 2017). Previous studies have demonstrated that PFAAs can be taken up
94 from contaminated soils, translocated and stored in different plant organs (Stahl et al.,
95 2009; Lechner and Knapp, 2011). Several experimental plots planted with maize, wheat
96 and vegetables in PFAA-spiked or bio-solids amended soils have indicated a
97 bioaccumulation potential of PFAAs. The bioaccumulation potential has been reported
98 to vary with PFAA concentrations in soil, functional group and chain length, soil
99 properties and plant species (Yoo et al., 2011; Blaine et al., 2013; Blaine et al., 2014a;
100 Wen et al., 2014; Krippner et al., 2015). However, to date, almost all studies on the
101 bioaccumulation of PFAAs in plants have been carried out in controlled plots or nutrient
102 solution experiments, which may not accurately reflect the weathered field conditions.
103 Risk assessments have confirmed that ingestion via diet is the most likely mechanism
104 for significant human exposure to PFAAs (D'Hollander et al., 2010; Vestergren et al.,
105 2012). This could occur from the consumption of crops grown in PFAA contaminated

106 soils or irrigated with contaminated water and precipitation (Blaine et al., 2014a; Wen
107 et al., 2014). In addition, the PFAAs contaminated crops can be used as fodder fed to
108 animals raised as food for humans and finally lead to human exposure of PFAAs
109 (Domingo, 2012; Kowalczyk et al., 2013).

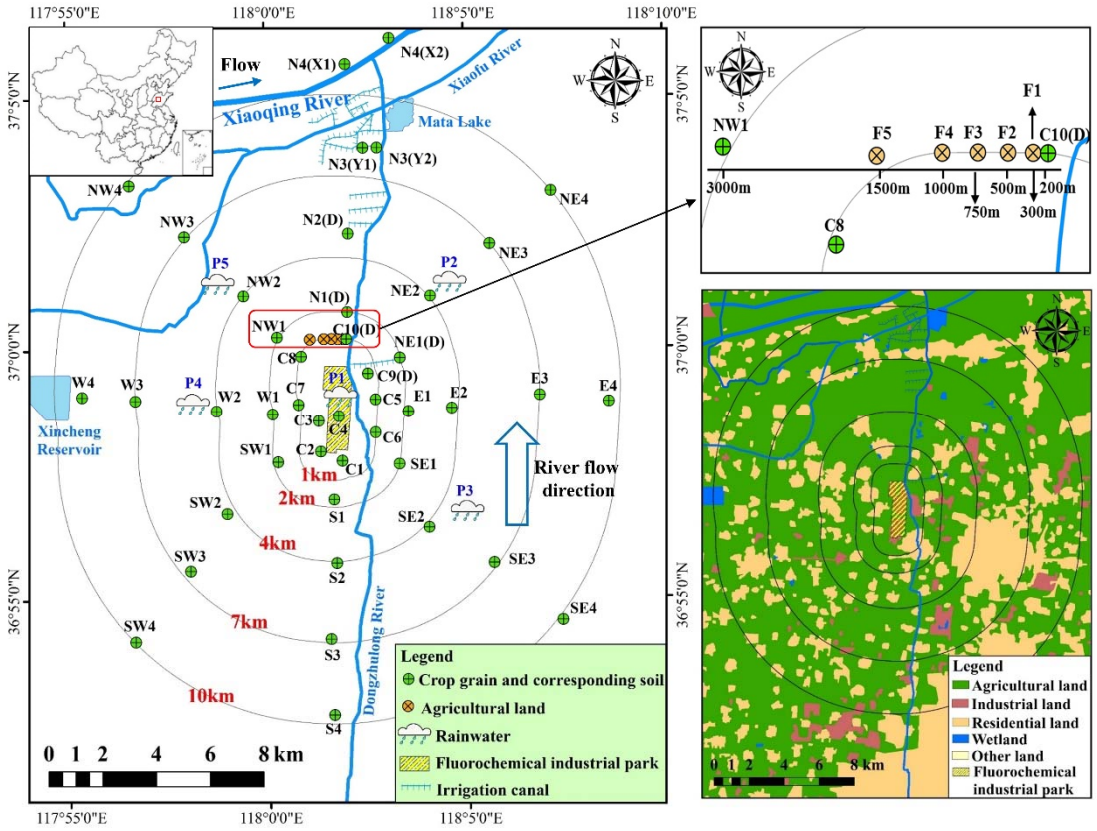
110 Restriction agreements on the production of PFAAs in Europe and America, such as
111 the 2010/2015 PFOA Stewardship Program and Stockholm Convention, have led to a
112 large number of PFAA-related industries transferred to developing countries including
113 China to meet the continuing demands (UNEP, 2009; USEPA, 2013). One such site is
114 the mega-fluorochemical industrial park (FIP) studied here, which is a production
115 center for PFAAs and fluoropolymers with an annual capacity of several hundred
116 thousand tons (Wang et al., 2016). PFAAs are usually used as processing aids during
117 production of fluoropolymers in the FIP, therefore PFAAs can be released to the
118 environment during direct production of PFAAs and fluoropolymers manufacturing
119 (Wang et al., 2014b). According to our investigation, PFAAs used in the FIP are
120 manufactured based on electrochemical fluorination, which was previously used by
121 major global producers. The linear PFAAs account for the vast majority of isomer
122 profiles of PFAAs, while the remaining is various branched isomers (Buck et al., 2011).
123 In this study, only linear PFAAs, the predominated isomer, were considered to analyze
124 the contamination and transport of PFAAs around the FIP. The FIP is located in an area
125 with large tracts of agricultural lands and scattered villages. Within a radius of 10km
126 from the FIP, a previous study has investigated the distribution and transport of PFAAs
127 in surface and ground water with the highest reported concentrations of 1,860 μg/L and

273 μg/L respectively (Liu et al., 2016). However, to systematically investigate multi-media contamination and transport of PFAAs from the FIP, PFAAs in other major media including soil, precipitation and crops needs to be studied. These results can then be associated with PFAAs present in local surface and ground water. Furthermore, the assessment of bioaccumulation of PFAAs in crops under weathered field conditions is of vital importance to produce a thorough risk assessment. This study provides an assessment of the multi-media transport of PFAAs from the FIP to soil followed by crop accumulation and consumption by local residents.

The objectives of this study were, therefore, to examine the contamination and risk from PFAAs around the FIP with particular emphasis on (i) geographic contamination patterns and decline processes for PFAAs in different environmental compartments, (ii) identification of transport pathways of PFAAs, (iii) assessment of bioaccumulation in locally produced wheat and maize, and (iv) conducting a human exposure estimation of PFAAs via consumption of local contaminated grains.

2. Materials and methods

2.1. Sampling design and collection



144

145 Fig.1 The map of the sampling locations for crop grain (wheat and maize), agricultural
146 soil, and rainfall collection around the FIP in Huantai County, Shandong Province,
147 China.

148 The study area surrounding the FIP is a major grain-producing region with large tracts
149 of agricultural lands and scattered villages, where wheat and maize provide the local
150 staple food source. With the FIP in Huantai County at the center, samples were collected
151 in central areas (C) within a radius of 1km and in eight directions (East, E; Southeast,
152 SE; South, S; Southwest, SW; West, W; Northwest, NW; North, N; Northeast, NE) and
153 this was repeated with increasing distances from the site of 2 km, 4 km, 7km, and 10
154 km. The 44 sample locations required the collection of mature wheat and maize grain
155 and corresponding soil samples (Fig. 1). In addition, some agricultural soil samples in

the transverse direction of the Dongzhulong River were also collected to study the influence of the contaminated river on PFAAs present in the soil. At each sampling site, wheat grains from 20 plants were randomly sampled from the center and four corners of an area of 10m × 10m, and mixed into one composite sample in June 2014. The corresponding surface soils (top 0-20cm) around each plant were collected at the same time with a stainless steel trowel that had been rinsed with methanol and mixed into one composite sample. Maize grain and their corresponding soils were also sampled in the same way in October 2014. The collected grain samples were wrapped in aluminum foil and stored in clean paper bags. Large stones and roots were removed from the soil samples with methanol rinsed tweezers before being sealed in polypropylene (PP) bags. According to the local wind frequency data in the recent twenty years, the primary downwind directions are west and northeast, followed by southeast while the minor downwind direction is northwest, and the calm wind frequency is also at high level (data from the Meteorological Bureau in Huantai County, Shandong Province, China). Based on the above information, 20 rainwater samples from 6 precipitation events were collected in pre-cleaned PP bottles close to the FIP and with a radius of 5km in the northeast, southeast, west and northwest from October to November in 2014. Rainwater parameters, including pH, dissolved oxygen, conductance and salinity, were determined in situ using a HQd Portable and Benchtop Meter Configurator (HACH Company, USA) (Table S1). All collected samples including grain, soil and rainwater were stored in an icebox during transport. The site information and ambient description are presented in Table S2.

After arriving at the laboratory, grain samples were washed carefully with Milli-Q water followed by distilled water before freeze-drying at a temperature of -50 ℃ for 48 h in a lyophilizer. A sample of 100 g was then ground and homogenized in a knife mill Grindomix GM 200 and then stored separately at -20℃ before analysis. To avoid cross-contamination during grinding, after each use, we cleared out the plant residue carefully, and then rinsed the mill with 5ml Milli-Q water for four times followed by 5ml 100% methanol for four times. Some previous detected wheat and maize grains with extremely low concentrations of PFAAs were used as procedure blanks to examine if cross-contamination occurred during grinding. The soil samples were transferred to PP boxes, dried in air, homogenized with a porcelain mortar and pestle, sieved with a 2 mm mesh, and stored in 250 mL PP bottles at room temperature until extraction. The total carbon (TC) and total nitrogen (TN) contents of the soil samples were determined using an Elemental analyzer (Table S3). The soil organic matter was measured using the Walkley–Black procedure (Nelson and Sommers, 1982) while pH was determined at a soil to 0.01 M $CaCl_2$ solution ratio of 1:5 (w/v) (Table S3). Rainwater samples were allowed to stand for 24 h to settle any sediment and then 400 mL of supernatant was taken from each sample for analysis. All these rainwater samples were extracted within 1 week after arrival in the lab, and the rest were stored at −20 °C for long-term reference.

2.2 Standards and Reagents

12 PFAAs in all samples were analyzed, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorobutane

sulfonate (PFBS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctane sulfonate (PFOS), perfluoroundecanoate acid (PFUdA), and perfluorododecanoic acid (PFDoA) and 9 mass-labeled PFAAs, containing $^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA,$^{13}C_4$PFNA, $^{13}C_4$PFDA, $^{13}C_4$PFUdA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS were purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada). More detailed descriptions on standards and reagents are available in the Supporting Information.

2.3 Extraction and cleanup

The rainwater, soil and plant samples were extracted mainly by solid phase extraction (SPE) using methods with minor modifications described previously by Taniyasu et al. (2005), Loi et al. (2011) and Felizeter et al. (2012) (Supporting Information). Individual PFAAs were separated and quantified using Agilent 1290 Infinity HPLC System equipped with an Agilent 6460 Triple Quadrupole MS/MS System (Agilent Technologies, Palo Alto, CA, USA) in the negative electrospray ionization (ESI) mode. The detailed descriptions of extraction and instrumental analysis are available in the Supporting Information and Table S4.

2.4 Quality Assurance and Quality Control (QA/QC)

In order to avoid cross contamination during field sampling, the outside of the bottles were washed with Milli-Q water after the samples were taken, wiped with a clean paper

220 towel and then kept in three-layers of sealed polyethylene bags. The soil samples were
221 kept in three-layers of sealed PP bags while grain samples were kept in three-layers of
222 sealed paper bags. Field blanks, transport blanks, procedure blanks and solvent blanks
223 were carried out with every sample set to examine if any external contamination
224 occurred during the sampling/extraction and analytical stages. The internal standard
225 calibration curve consisted of a concentration gradient (0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50,
226 and 100 ng/mL) of native standards, spiked with a 5 ng internal standard. These were
227 solvent based standard curves and not matrix matched extracted calibration curves. This
228 was prepared for quantification of the individual PFAA with coefficients (r^2) for all
229 target analytes exceeding 0.99. The limit of detection (LOD) and limit of quantification
230 (LOQ) were defined as the peak of analyte that needed to yield a signal-to-noise (S/N)
231 ratio of 3:1 and 10:1, respectively. When the concentrations of PFAAs in any extract
232 that was greater than 100 ng/mL, the volume or amount of the samples would be
233 reduced and the samples would be extracted again to fit the range of the calibration
234 series. The different matrices were spiked with a standard solution and then analyzed
235 to determine the recovery of each target PFAA. The matrix spike recoveries (MSRs)
236 ranged from 79% to 109% for rainwater, 72% to 93% for soil and 66% to 102% for
237 plant material. Supporting Information and Table S5 describe detailed QA/QC
238 information.

239 *2.5 Statistical and spatial analyses*

240 Statistical analysis was performed using SPSS Statistics V22.0 (SPSS Inc. Quarry Bay,

HK). During the analysis, concentrations less than the LOQ were set to one-half of the LOQ, and those less than the LOD were assigned to values of LOD/$\sqrt{2}$ (Hornung and Reed, 1990; Bao et al., 2011; Wang et al., 2014). Spatial distributions of PFAAs were analyzed using the symbology tools including features, charts and multiple attributes in the ArcMap module of ArcGIS V10.2 software (ESRI, Redland, CA, USA).

2.6 Bioaccumulation Metrics and Daily Intake Estimation

Soil and grain samples in the study were dried before extraction and analysis of PFAAs, therefore all concentration values of PFAAs in soil and grain are based on dry weights. The bioaccumulation factors (BAFs), defined as ratios between the chemical concentration determined on a dry weight basis in the grain and corresponding soil, were calculated by Eq. (1) (Blaine et al., 2013). Due to the low volatility of PFAAs in the environment, PFAAs entry into the stomata from the air was considered negligible and all these substances in grain were assumed to be derived from uptake through the roots.

$$BAF = \frac{PFAA\ concentration\ in\ grain\ (ng/g\ dw)}{PFAA\ concentration\ in\ soil\ (ng/g\ dw)} \quad \text{Eq. (1)}$$

$$EDI = \frac{Daily\ consumption\ (g/d\ dw) \times PFAA\ concentration\ in\ grain\ (ng/g\ dw)}{Body\ weight\ (kg)} \quad \text{Eq. (2)}$$

The estimated daily intake (EDI, ng/kg·bw/day) of PFAAs through the consumption of wheat and maize can be calculated based on averaging the intake dose by body weight by Eq. (2). Further details are contained in Table S6. Considering that body weights and consumption rates vary by age, the EDIs were estimated for four age

groups: toddlers (2-5 years), children (6-10 years), teenagers (11-17 years), and adults (≥18 years) (Zhai, 2008; Zhang et al., 2010). As for the EDI calculation for residents with different radius from the FIP, the average concentrations of PFAAs in wheat and maize grain collected in that radius were used.

3. Results and discussion

3.1 Multi-media distribution and transport of PFAAs around the FIP

3.1.1 Occurrence and distribution of PFAAs in agricultural soil

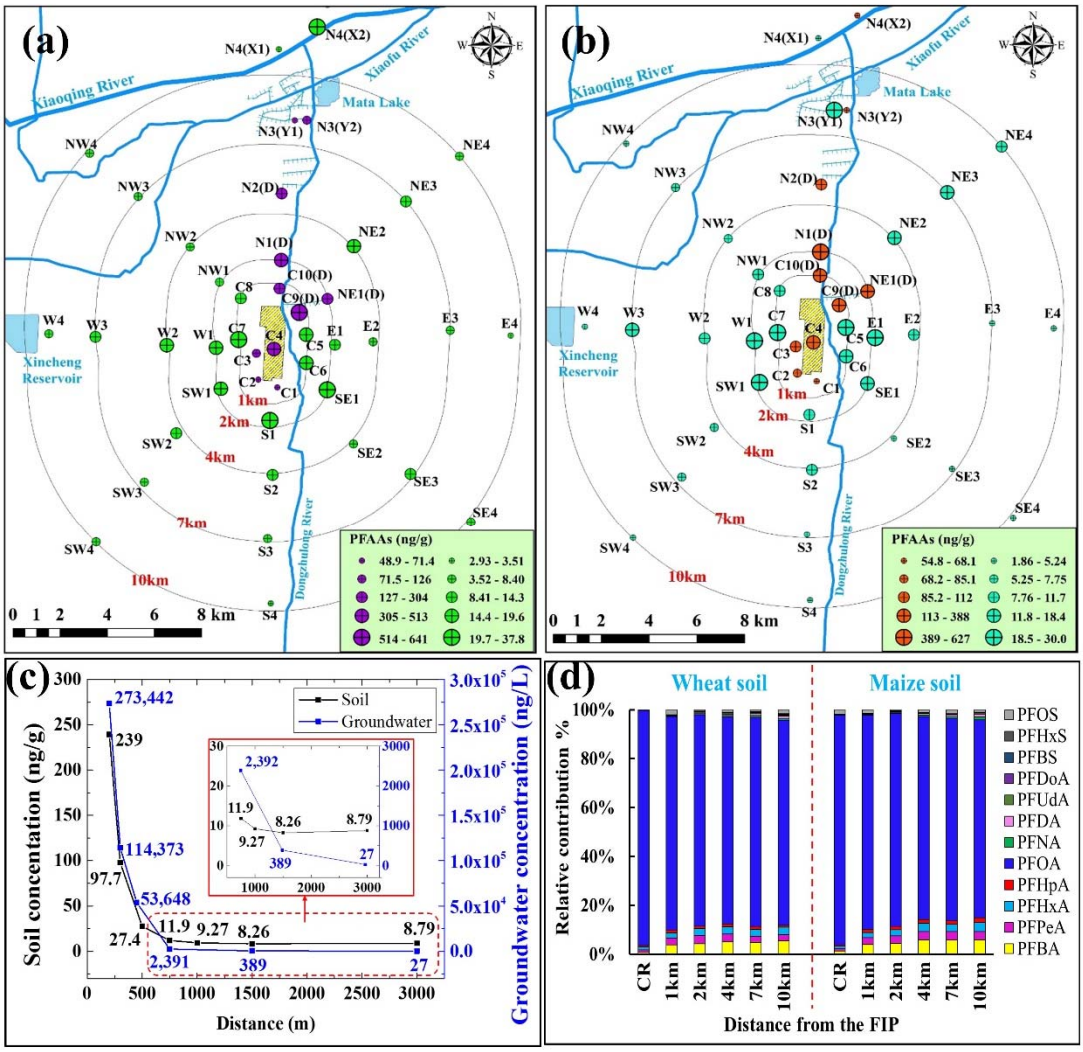


Fig. 2 The spatial distribution of ∑PFAAs and relative contribution of individual PFAA in agricultural soil with the increase in distance from the FIP [(a) and (c)]; the decline curve of ∑PFAAs in agricultural soil and groundwater with distance from the polluted river (b).

Note: CR represents contaminated riverfront along the wastewater river, the same as below; due to the large variation of PFAA concentrations in soil, dual scales with two different colored circles were used in each figure (a, b) to show the spatial distribution of PFAAs.

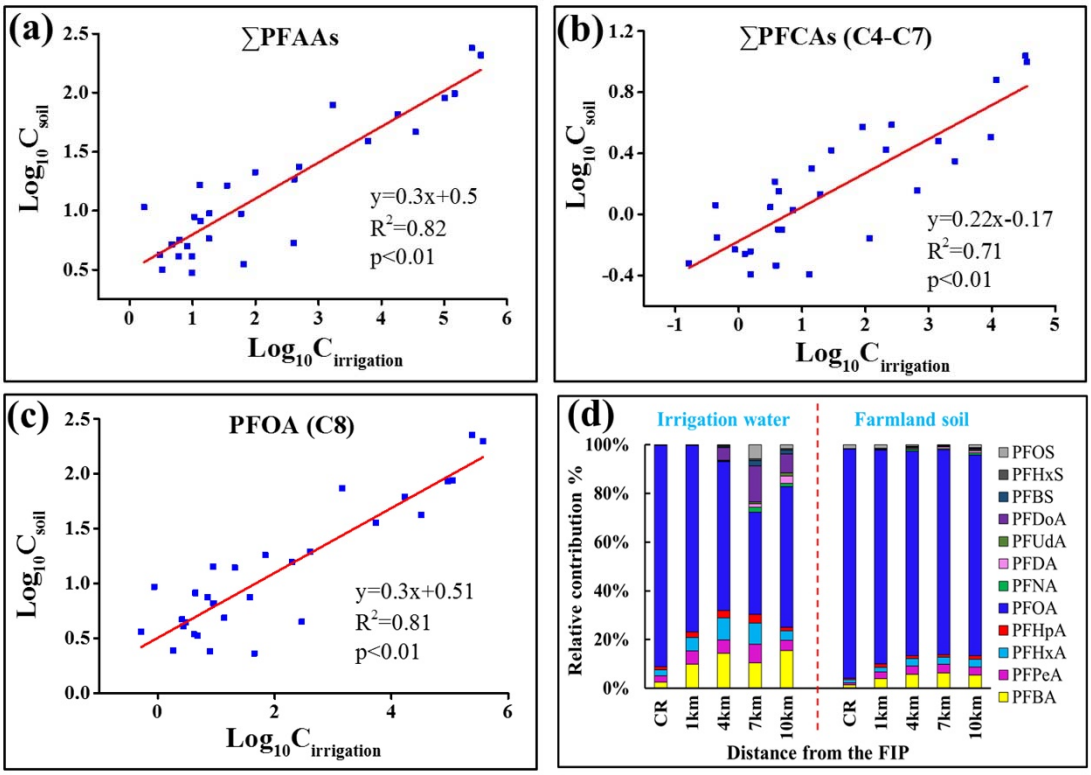
The concentration of the sum of PFAAs (∑PFAAs) ranged from 1.86 ng/g to 641 ng/g in agricultural soils (Table S7-S8). Of the PFAAs, PFOA was the dominant component with an average contribution of 86% of the ∑PFAAs, followed by C4-C7 short-chain perfluoroalkyl carboxylic acids (PFCAs) including PFBA (4.2%), PFPeA (2.7%), PFHxA (2.5%) and PFHpA (1.2%). Long-chain PFCAs (C9-C12) and perfluoroalkane sulfonic acids (PFSAs) including PFBS, PFHxS and PFOS were only observed at low concentrations or below the LOD, which is most likely to be related to their limited production and application of these components in this region (Wang et al., 2014a; Wang et al., 2016). In most sampling locations, the concentration and composition of PFAAs in wheat soil showed no significant differences from those in maize soil (Independent samples T-test, $p>0.05$; $n=44$). To the best of our knowledge, the maximum PFOA concentration in agricultural soil (623 ng/g) reported in this study is the highest ever reported, which even exceeded soil receiving industrially contaminated

bio-solids as a soil amendment at 320 ng/g (Washington et al., 2010). Previous studies of the area have confirmed the FIP as the only point source in the area, which included not only PFCA production but also fluoropolymer manufacturing and processing (Liu et al., 2016). Global source inventories demonstrated that releases of PFCAs are largely attributed to these industrial processes (Wang et al., 2014b). Furthermore, the increasing concentrations of PFAAs in soil with proximity to the FIP also supported it as the principal source.

The contamination hotspots of PFAAs in soil were found near the FIP and the Dongzhulong River, which receives wastewater from the FIP. As the distance increased from these sources, the levels of PFAAs in soil decreased with an exponential trend, showing a sharp initial decrease followed by a gentle decline. The average concentrations of ∑PFAAs in wheat soil within 1km from the FIP was up to 88.7 ng/g, then sharply decreased by about 81% to 16.8 ng/g at 2km and further fell by 13.4% to 4.94 ng/g within the distance of 2-10km; while those in maize soil within 1km were up to 91 ng/g, then reduced by 79% to 19 ng/g at 2km and then slowly decreased by 16% to 4.41 ng/g within the distance of 2-10km (Fig. 2a). For soil along the lateral direction from the Dongzhulong River, the concentration of ∑PFAAs also rapidly dropped by 95% (from 239 ng/g to 11.9 ng/g) within a distance of 200-750m, then declined by 1.3% to 8.79 ng/g within a distance of 750-3000m (Fig. 2b). Influenced by the presence of the FIP, even the lowest concentrations of ∑PFAAs detected at a distance of 10km were still above most reported soil concentrations in China (reviewed in Table S9). With the increasing distance from the FIP, the shorter-chained PFAAs (C4-C6) increased in

312 proportion to PFOA (C8) in soil, due to the potential for enhanced volatility and
313 mobility of shorter-chained PFAAs in the environment (Ahrens et al., 2009; Ferrey et
314 al., 2009). PFAAs in agricultural soil may be associated with residues in local surface
315 and ground waters, which also showed a similar decline in concentration and
316 compositional change (Liu et al., 2016). The confluence of the effluent from the FIP
317 with the Xiaoqing River resulted in PFAAs concentrations that increased by 2-3 orders
318 of magnitude, while the concentrations in agricultural soil irrigated by the river also
319 increased by about 12 times. Compared to those in river water for irrigation, PFOA and
320 other longer-chained PFCAs in soil accounted for higher proportions of the total PFAAs
321 (Fig. 3d). The stronger adsorption to soil and less mobility for long-chained PFAAs
322 contributed to the soil accumulation of these chemicals from irrigation, dry and wet
323 deposition. In addition, it was noted that higher concentrations of PFAAs in the
324 agricultural soil were also found primarily on the downwind (i.e. west and northeast)
325 side of the FIP, implying another likely contamination pathway through atmospheric
326 emission, transport and local deposition (Davis et al., 2007) (Fig. S1). Moreover, soil
327 erosion caused by wind is also considered as an important factor in the spatial trend of
328 PFAAs, showing movement downwind.

329 *3.1.2 Pollution association of PFAAs in irrigation water and agricultural soil*



330

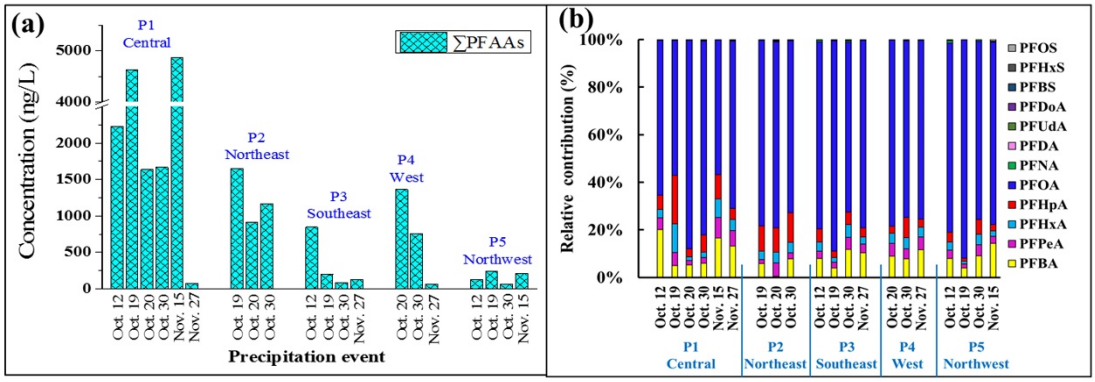
331 Fig. 3 The relationship (a, b, c) between PFAAs, PFCAs and PFOA found in agricultural
332 soil and corresponding irrigation water and the different profiles (d) of PFAAs in
333 agricultural soil and irrigation water.

334 Note: $C_{irrigation}$ represents concentrations of PFAAs in irrigation water; C_{soil} represents
335 concentrations of PFAAs in agricultural soil.

336 The contamination of PFAAs in local surface and ground water, which are mainly used
337 as irrigation water for agricultural lands, has been investigated in a previous study (Liu
338 et al., 2016). Combining these results, the contamination associated PFAAs in
339 agricultural soils and irrigation water will be discussed further. For ∑PFAAs and
340 several main PFAA components, there was a significant linear positive correlation
341 between the logarithm of concentrations in agricultural soils and corresponding

342 irrigation water (Fig. 3a, 3b and 3c). Thus, contaminated irrigation water was
343 considered as an important input of PFAAs in agricultural soils. However, it is worth
344 mentioning that the increases for longer-chain PFAAs yielded steeper slopes compared
345 to those for shorter-chain homologues (Fig. 3b, 3c; Table S10). This phenomenon can
346 be explained by stronger adsorption to soil by longer-chain PFAAs (Higgins and Luthy,
347 2006). With higher aqueous solubility and lower adsorption affinity (Ahrens et al., 2009;
348 Ferrey et al., 2009), shorter-chained PFAAs present in irrigation water are more likely
349 to leach through the soil profile compared to the more hydrophobic components.
350 Therefore, short-chain PFAAs were present at lower proportions in agricultural soils
351 than those in corresponding irrigation water (Fig. 3d).

352 *3.1.3 PFAAs levels and composition in precipitation*



353

354 Fig. 4 The concentrations (a) and composition (b) of PFAAs in rainwater collected near
355 the FIP.

356 As the most effective atmospheric removal mechanism for PFAAs (Taniyasu et al.,
357 2013), rainwater was collected to examine the importance of local precipitation as a
358 source of soil contamination near the FIP. High levels of PFAAs were found in

359 rainwater within 5km from the FIP with the concentrations of 60 to 4,862 ng/L (Fig. 4a;
360 Table S11). PFOA was predominant with the average relative contribution of 76%,
361 followed by PFBA (8.9%), PFHpA (6.6%), PFHxA (4.1%) and PFPeA (4.1%) (Fig. 4b).
362 The maximum concentration of PFOA (2,752 ng/L) found here was the highest ever
363 reported in precipitation, which far exceeded high values previously reported such as
364 in Tianjin (107 ng/L) and Dalian (65.8 ng/L) of China, in Yokohama (95.3 ng/L) of
365 Japan, in Albany (23.9 ng/L) of the USA and in the northern regions (45.5 ng/L) of
366 Germany (reviewed in Table S12). These contamination levels of PFAAs in rainwater
367 reported in this study were comparable to those in house dust (73-13,500 ng/g) and
368 street dust (5-9,495 ng/g) around this FIP, which were likely from dry deposition (Su et
369 al., 2016). High levels of PFAAs in both rainwater and dust around the FIP confirmed
370 it as the important source of local air emission of PFAAs. The airborne PFAAs released
371 from these manufacturing and use facilities were found to be mostly combined with
372 particulate matters (Barton et al., 2006; Harada et al., 2006; Shan et al., 2015), which
373 have limited long-ranged transport potential and are easily removed by precipitation
374 (McMurdo et al., 2008; Mader, 2009).

375 The levels of PFAAs in rainwater sharply reduced with distance from the FIP,
376 especially for short-chained PFCAs and PFOA. The highest levels of PFAAs associated
377 with precipitation occurred immediately around the FIP with an average concentration
378 of 2,265 ng/L, but rapidly decreased by 45%-93% within only 5km. Other high
379 concentrations of PFAAs in rainwater were found in the northeast (average 1,241 ng/L)
380 and west (average 513 ng/L) of the FIP, followed by those in southeast (average 315

ng/L) and northwest (average 161 ng/L). This would be expected on the basis of the prevailing wind in the area (Barton et al., 2006). PFAAs levels in house and street dust around the FIP mainly from dry deposition followed a similar trend (Su et al., 2016).

3.2 Crop grain contamination and bioaccumulation of PFAAs around the FIP

3.2.1 Occurrence of PFAAs in wheat and maize grain around the FIP

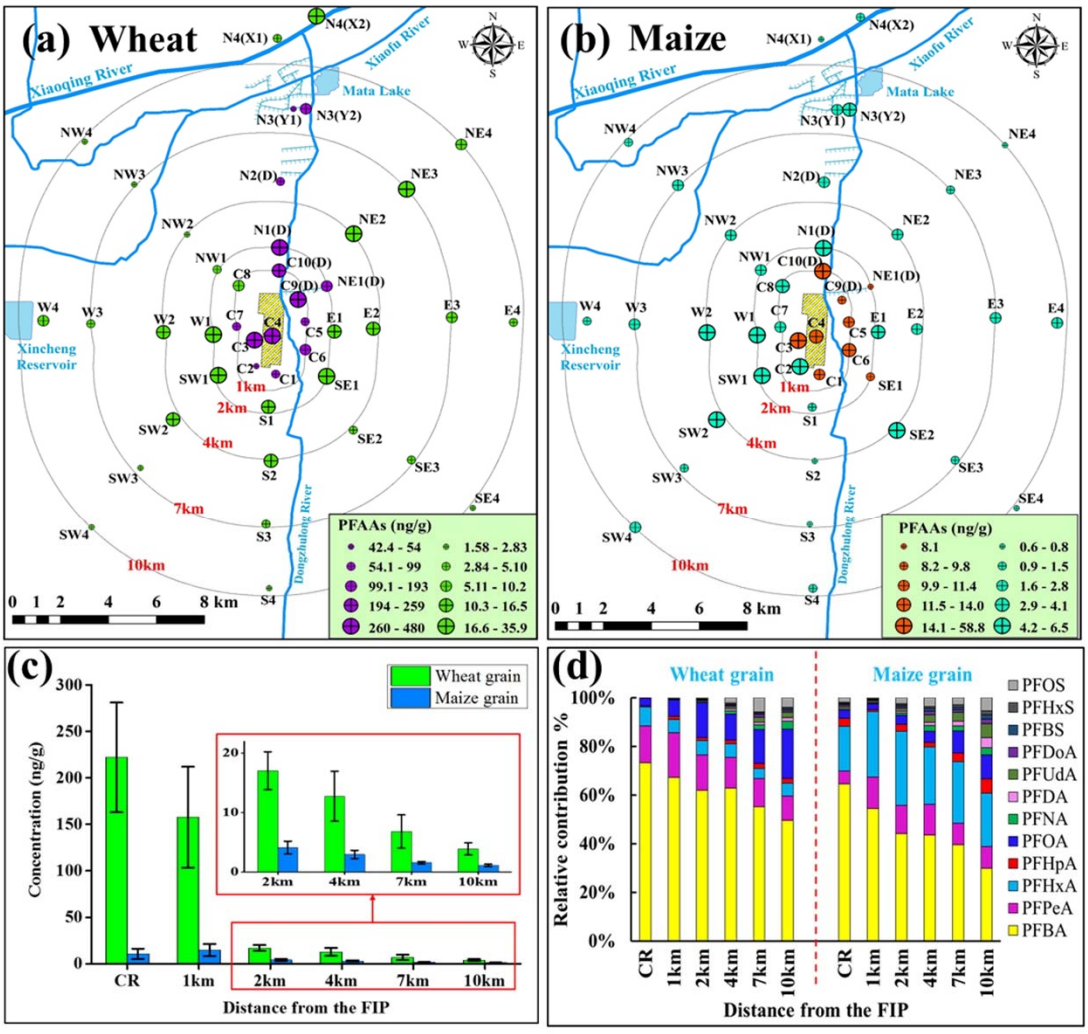


Fig. 5 Spatial distribution (a, b), decline process (c), and profiles (d) of PFAAs in wheat and maize grain with the increasing distance from the FIP.

389 Note: Due to the large variation of PFAA concentrations in grain, dual scales with two
390 different colored circles were used in each figure (a, b) to show the spatial distribution
391 of PFAAs.

392 The concentrations of ∑PFAAs ranged from 1.13 ng/g to 480 ng/g in wheat grain and
393 from 0.7 ng/g to 58.8 ng/g in maize grain within 10 km of the FIP (Table S13-S14).
394 Unlike irrigation water, agricultural soil and precipitation, short-chained PFCAs (C4-
395 C7) were the major PFAA components in wheat and maize grains, indicating there must
396 be a bioaccumulation preference for these homologues (Krippner et al., 2014; Wen et
397 al., 2014). In the case of the grain, PFBA was the dominant form, representing, on
398 average, 61% in wheat grain and 46% in maize grain of the total PFAAs (Fig. 5d).
399 Long-chained PFCAs (C9-C12) and PFSAs were only found in trace amounts or below
400 the LOD. Compared to wheat grain, maize grain showed stronger bioaccumulation
401 tendency for PFHxA and PFHpA.

402 PFAAs concentrations in grains also showed a sharp decrease in a short distance from
403 the FIP, followed by a gentle decline. The average concentrations of ∑PFAAs in wheat
404 grain within 1km from the FIP were as high as 161 ng/g, rapidly reducing by 89% to 17
405 ng/g at 2km followed by slower decrease by 6.9% to 5.94 ng/g within the distance of 2-
406 10 km; while residues in maize grain within 1km were up to 76 ng/g, although falling
407 sharply by 94% to 4.34 ng/g at 2km with a further slower decline by 3% to 2.09 ng/g
408 within the distance of 2-10 km (Fig. 5c). Contamination hotspots of ∑PFAAs present in
409 grains were also associated with plants grown along the banks of the heavily polluted

Dongzhulong River (Liu et al., 2016), with average concentrations of 223 ng/g for wheat grain and 10.5 ng/g for maize grain. Within the study area, ∑PFAAs levels in wheat grain were typically 11.3 fold higher than those in maize grain (Fig. 5a, 5b), which may be attributed to stronger PFAA bioaccumulation potential for wheat grain (Wen et al., 2014; Krippner et al., 2015).

3.2.2 Crop bioaccumulation of PFAAs around the FIP

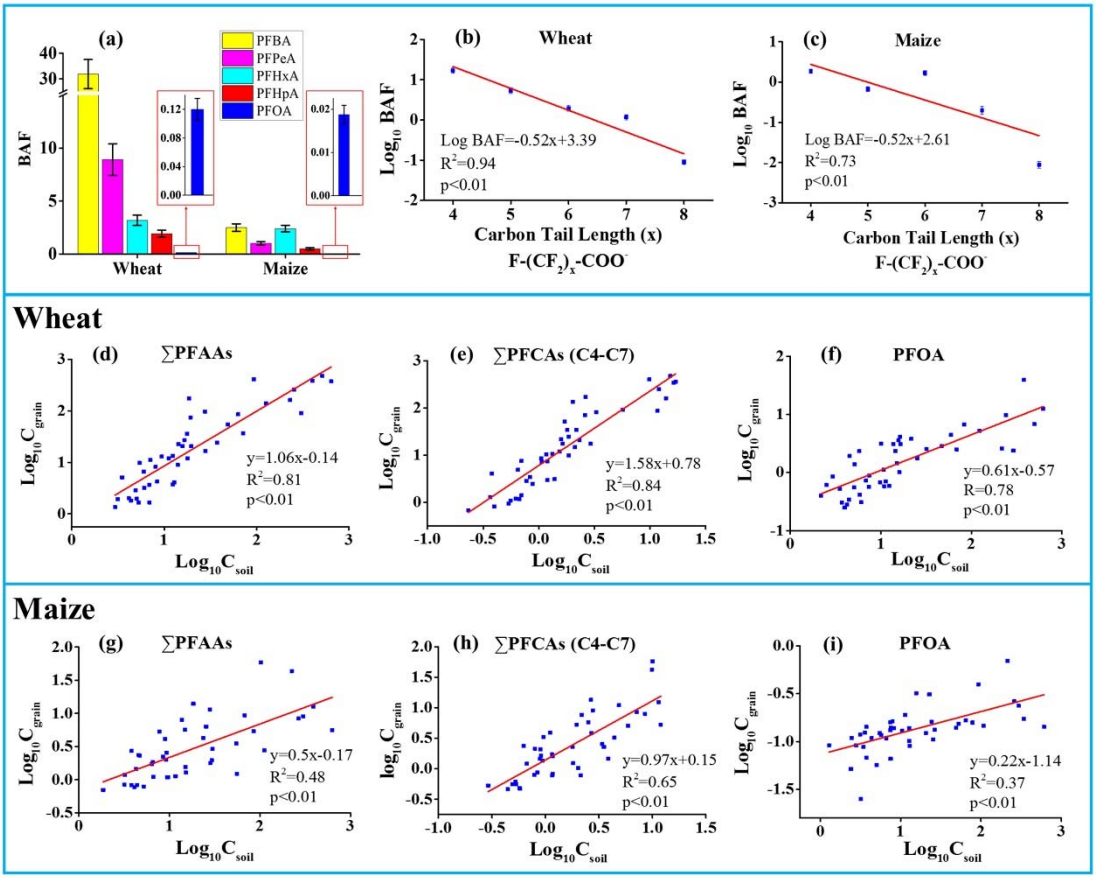


Fig. 6 BAFs for several major PFCAs (a), correlations between log BAF and carbon chain length (b, c), and bioaccumulation equations of PFAAs (d-i).

Soil properties such as organic matter content (20.2±3.79 g/kg) and pH (7.84±0.26) across the study area were relatively similar (including both wheat and maize growing areas) (Table S3). The bioaccumulation factors (BAF) for ∑PFAAs in wheat grain were typically 11.6 times higher than those in maize grain (Fig. 6a). The uptake and migration of PFAAs in plant mainly depended on transpiration stream (Blaine et al., 2013; Blaine et al., 2014b). The transpiration coefficients for wheat (450-600) are generally higher than those for maize (250-300), which may contribute to higher BAFs for PFAAs in wheat grain (IGSNRR, 2006). In addition, the phenomenon may also be related to the higher protein contents in wheat gain (14.1%) than those in maize grain (10.6%) (Zhang, 1997; Wang et al., 2003). Previous studies have found the high affinity of PFAAs to proteins and further confirmed the effect of protein content on the accumulation of PFAAs in plants (Bischel et al., 2011; Wen et al., 2016; Xia et al., 2013).

In the wheat and maize grain, total concentrations of shorter-chained PFCAs (C4-C7) were about 20-fold and 33-fold larger, respectively, than those of PFOA, despite the soil concentrations of PFOA being more than an average of 19 times that of the shorter-chained PFCA concentrations. The significant contrast of PFAA profiles in grain and soil were mainly caused by crop bioaccumulation preference for short-chain PFAAs. In fact, the BAF for wheat and maize grain showed a decreasing tendency with increasing chain length. PFBA (C4) showed the highest BAFs averaging 33.1 for wheat grain and 2.5 for maize grain while PFOA showed the lowest values averaging 0.12 for wheat grain and 0.02 for maize grain (Fig. 6a). The $\log_{10}$ BAFs for wheat and maize grain were correlated with carbon chain length for several major PFCAs. The BAFs in both

grains decreased by approximately 0.5 log units per CF_2 group for these PFCAs (Fig. 6b, 6c). Similar results are also reported in vegetables, and the BAFs of PFAAs for lettuce, tomato and pea in greenhouse decrease approximately 0.3, 0.5 and 0.6 log units per CF_2 group (Blaine et al., 2013; Blaine et al., 2014b). The higher BAFs for shorter-chain PFAAs may be related to their lower sorption by soil particles and smaller molecular size (Higgins and Luthy, 2006). This would have the effect of greater availability to the plants as well as to a higher mobility and translocation rate within the plants (Felizeter et al., 2012; Felizeter et al., 2014; Krippner et al., 2014).

The uptake and storage of PFAAs in wheat and maize grain unsurprisingly had a link with agricultural soil concentrations. For Σ PFAAs and several main PFAA components, the logarithms of concentrations in agricultural soil and grain showed significant linear positive correlations ($p<0.01$) (Fig. 6). However, the slopes of soil-grain equations, which were closely associated with BAF, also showed a declining trend with the increase of carbon chain length (Table S15). When soil concentration increased, a steeper slope for short-chain PFCAs would result in a greater concentration increase in grain. This can explain the proportional increase of short-chain homologues in grains with proximity to the FIP. Moreover, higher slopes in soil-wheat equations than soil-maize equations further confirmed stronger bioaccumulation potential for wheat grain.

3.3 Human exposure estimation of PFAAs for local residents

Some high concentrations of PFOA in agricultural soil near the FIP and along the heavily polluted Dongzhulong River exceeded the predicted non-effect concentration

(PNEC) of 160 ng/g (Amundsen et al., 2008), indicating a potential ecological risk to soil organisms. However, such soil levels were still much lower than the residential soil screening level (16,000 ng/g for PFOA) recommended by the USEPA, indicating that health risk via ingestion, inhalation and dermal exposure of contaminated soil would be very low (USEPA, 2014). However, an exposure pathway for PFAAs of greater concern for human health would be through the diet (Vestergren et al., 2012). In the study area, wheat and maize account for 73% and 7%, respectively, of staple food, and most local residents consume their grains from their own cereal crops (Bureau of Statistics of Shandong Province, China, 2015). The EDIs of PFAAs for different age groups via consumption of contaminated wheat and maize grain were calculated to assess health risks to local residents (Table S16-S17).

For local residents, the EDIs of PFAAs through wheat consumption was about 83 times higher than that through maize consumption (Table S16). The EDIs of major PFAA components via consumption of wheat and maize varied, depending on the distance and the age group of the residents living around the FIP (Table S17). Consistent with PFAAs distribution in grains, the highest EDIs of PFAAs for the different age groups occurred within 1km from the FIP and along the river receiving the wastewater discharge. For residents within 1 km from the FIP, the average exposure of ΣPFAAs via consumption of these grains were estimated to be 1,219 ng/kg·bw/day for toddlers and 1,228 ng/kg·bw/day for children, followed by teenagers (934 ng/kg·bw/day) and adults (828 ng/kg·bw/day) (Table S17). Similar high values of EDI were also found to be 998 ng/kg·bw/day for adults near a PFAAs production facility in Hubei Province, China,

485 which further confirmed that PFAAs-related facilities were important sources of high
486 human exposure of PFAAs for nearby residents (Zhang et al., 2017). As expected, for
487 major components and ∑PFAAs in all sampling locations of this study, the EDI for
488 toddlers and children were also comparable, but both higher than those for teenagers
489 and adults. The higher food consumption per body weight for toddlers and children
490 compared to teenagers and adults can explain this difference (Klenow et al., 2013).
491 Similar results were also found in China from consumption of meat and eggs with
492 PFOA EDIs of 15.9 to 19.7 ng/kg·bw/day for toddlers and 7.75 to 10.5 ng/kg·bw/day
493 for adults (Zhang et al., 2010), and in Belgium through multiple foodstuffs with PFOA
494 EDIs ranging from 0.28 to 0.39 ng/kg·bw/day for children and 0.19 to 0.23
495 ng/kg·bw/day for adults (Klenow et al., 2013).

496 As far as we are aware, the tolerable daily intake (TDI) values are only available for
497 PFOA. Compared to current recommended TDI values of 100 to 1,500 ng/kg·bw/day
498 for PFOA proposed by several countries (Fig.7), the EDI of PFOA via consumption of
499 wheat and maize alone for residents in the study area are less than these thresholds.
500 However, it is noteworthy that the EDI values of PFOA via wheat and maize
501 consumption for toddlers (72.3 ng/kg·bw/day), children (72.8 ng/kg·bw/day), teenagers
502 (55.4 ng/kg·bw/day), adults (49.2 ng/kg·bw/day) within 1km from the FIP were close
503 to the TDI value of 100 ng/kg·bw/day recommended by the Federal Environment
504 Agency, Germany (TWK, 2006) (Fig. 7). Besides consumption of wheat and maize
505 grain, other exposure pathways exist. Groundwater is used as a source of local drinking
506 water, and at this location PFOA levels in groundwater within a radius of 1km from the

FIP were up to 1-4 orders of magnitude higher than the Health Advisory (HA, 70 ng/L) recommended by the USEPA (USEPA, 2016; Liu et al., 2016). Within 2km from the FIP, the EDIs of PFOA via dust ingestion and dermal absorption has also been estimated to be 26 ng/kg·bw/day for toddlers, 10.5 ng/kg·bw/day for children, 5.52 ng/kg·bw/day for teenagers and 4.42 ng/kg·bw/day for adults (Su et al., 2016). Moreover, consumption of potentially contaminated vegetables and fruits, also grown in the area, although not studied here, may also contribute to the dietary load. When combined with these exposure pathways, the EDIs of PFOA for residents, especially toddlers and children, within 1km from the FIP are likely to exceed the TDI value of 100 ng/kg·bw/day from Germany, indicating a potential human health risk. Residents along the Dongzhulong River downstream of the FIP were exposed to the next highest level of PFOA-contaminated soil and water.

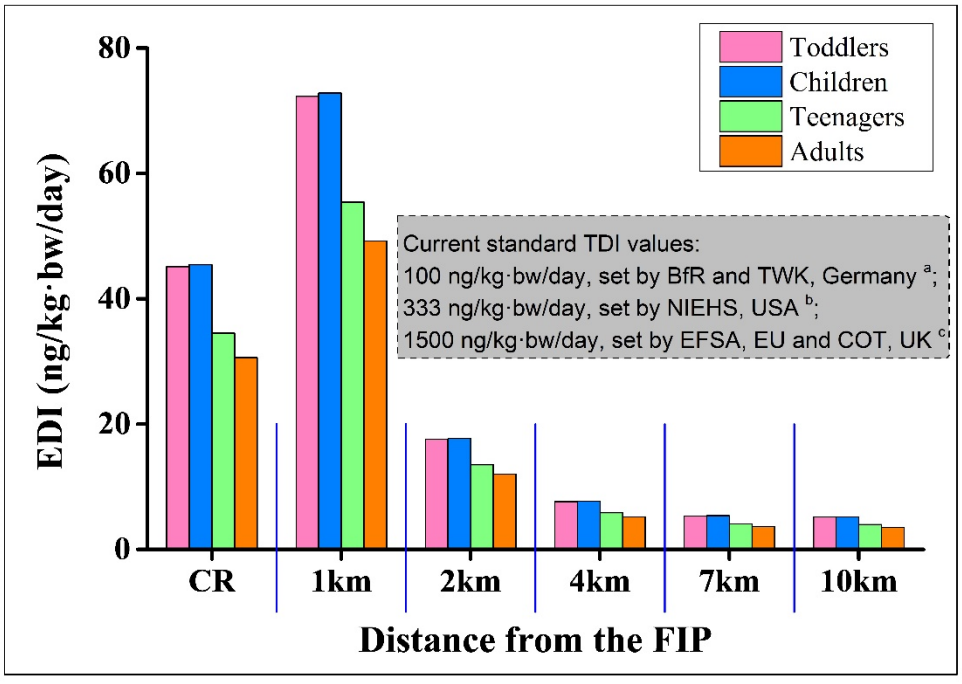


Fig. 7 Estimated daily intakes (EDI) of PFOA via consumption of wheat and maize

(ng/kg·bw/day) for various age groups.

Note: (1) a, the tolerable daily intake (TDI) value of 100 ng/kg·bw/day is derived from BfR (2006) and TWK (2006); b, the TDI value of 333 ng/kg·bw/day is derived from Thayer and Houlihan (2002); c, the TDI value of 1500 ng/kg·bw/day is derived from Benford et al. (2008) and COT (2009). (2) The detailed explanations about the calculation methods of above TDI values of PFOA referred in the study have been shown in the Supporting Material (Line 173-220).

The EDIs of PFOA for adults via dietary intake from multiple food sources have been reported in China (7.75-10.5 ng/kg·bw/day) (Zhang et al., 2010), Japan (0.72-1.3 ng/kg·bw/day) (Kärrman et al., 2009), Germany (2.9 ng/kg·bw/day) (Fromme et al., 2007), the US (0.82 ng/kg·bw/day) (Schecter et al., 2010), Norway (0.42 ng/kg·bw/day) (Haug et al., 2010) and Sweden (0.35-0.69 ng/kg·bw/day) (Vestergren et al., 2012). Unquestionably, the EDIs of PFOA (adults: 49.2 ng/kg·bw/day) reported in this study were higher than those values previously reported. Even at 10km away from the FIP, the EDIs of PFOA (adults: 3.51 ng/kg·bw/day) via the consumption of wheat and maize only were still comparable or higher than the upper limits of most reported EDI values, indicating the effective distance of the FIP for crops was at least 10km. These considerations are only for PFOA, which is only one component of the PFAA family. Crop bioaccumulation preference results in the EDIs of shorter chained PFCAs for residents being much higher than those for PFOA (Zhang et al., 2017). However, the health risk of these short-chain homologues cannot be assessed due to shortage of their

TDI values, which was a result of a paucity of human and ecological toxicological data for these chemicals (USEPA, 2017). So health risk from consumption of PFAAs in wheat and maize crops for local residents may go further than just PFOA. Moreover, PTFE production has been expanded in the FIP with an average annual growth rate of 25% since 2001 (Wang et al., 2016). If without suitable substitutes for PFAAs in the production of most fluoropolymers or improvement in the 'quality' of local food sources, local residents may face continuous or even higher exposure.

4. Conclusions and perspectives

Overall, the results of this study indicate that:

- The highest concentrations of ∑PFAAs in agricultural soil were observed near the FIP (max 402 ng/g) and along the banks of the FIP effluent dominated river (max 641 ng/g). As the distance increased from these sources, PFAAs levels in soil showed a sharp initial decrease followed by a slower decline. Higher PFAAs concentrations in agricultural soil showed positive correlation with the prevailing wind direction.

- The use of contaminated irrigation water and the influence of contaminated precipitation are two of the dominant pollution pathways of PFAAs to agricultural soil. Longer-chained PFAAs in irrigation water were more susceptible to adsorption to soil particles. For precipitation, unprecedented levels of ∑PFAAs were found immediately near the FIP with an average concentration of 2,265 ng/L, although they decreased sharply beyond 5km. In these abiotic media, PFOA (C8)

563 was the predominant PFAA, followed by shorter-chained PFCAs (C4-C7).

564 - A pollution signal from the FIP could be found as far away as 10 km within cereals
565 with concentrations ranging from 1.13-480 ng/g in wheat grain to 0.7-58.8 ng/g in
566 maize grain. The hotspot distribution and decline process of ∑PFAAs in grain
567 were similar to those in soil. The shorter chain varieties such as PFBA (C4) were
568 accumulated by these crops preferentially, accounting for an average of 61% in
569 wheat grain and 46% in maize grain, followed by other short-chained PFCAs (C5-
570 C7) and PFOA (C8).

571 - The uptake and storage of PFAAs in wheat and maize grain showed a decreasing
572 tendency with the increase of carbon chain length and the BAFs in both grains
573 decreased by approximately 0.5 log units per CF_2 group. The BAF of ∑PFAAs in
574 wheat grain were on average 11.6 times higher than those in maize grain, which
575 may be linked to higher protein contents in wheat grain. Significant linear positive
576 correlations were found between the logarithms of PFCA (C4-C8) concentration in
577 agricultural soil and grain.

578 - High concentrations of PFOA in agricultural soil may lead to potential soil
579 ecological risks. Consumption of contaminated grain grown within a radius of 1km
580 from the FIP and downstream of effluent dominated river could have impacts on
581 human health. The group most at risk would be toddlers and children due to their
582 weight relative to exposure.

583 - Based on crop bioaccumulation preference for short-chained PFCAs, it may be

584 worthwhile to consider whether it is desirable to substitute longer-chain PFAAs
585 with shorter-chain compounds in industrial processes. Therefore, more
586 toxicological studies on short-chained PFAAs are urgently needed for a more
587 comprehensive assessment of health and ecological risks. Moreover, further
588 consideration is also required for hazards of consuming aquatic products, livestock
589 and poultry, tuber crops, and various vegetables contaminated by these chemicals.
590 In addition, the accumulation and bio-magnification of the PFAAs into insects,
591 birds and small mammals should also be considered to study ecological hazards of
592 PFAAs to local species.

593 ● This study has linked the high local contamination with polluted wastewater
594 discharge from the FIP and airborne emissions. These sources could potentially be
595 reduced with granular activated carbon wastewater treatment plants and an exhaust
596 gas purification system (Hintzer et al., 2006; Rumsby et al., 2009). In addition,
597 non-fluorinated alternatives that are neither persistent nor toxic should be also
598 developed to eliminate the PFAA risk from the source.

599

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Supporting Information

Crop bioaccumulation and human exposure of perfluoroalkyl acids through multi-media transport from a mega fluorochemical industrial park, China

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Figure S1 The concentrations of PFAAs in wheat and maize soil in different directions and their corresponding wind frequencies.

References

Standards and Reagents

A total of 12 native PFAAs, containing perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) and 9 mass-labeled PFAAs, containing $^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA,$^{13}C_4$PFNA, $^{13}C_4$PFDA, $^{13}C_4$PFUdA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS were purchased from Wellington Laboratories with purities of >98% (Guelph, Ontario, Canada). Mixed standards were prepared in 100% methanol and stored at 4 ℃. Methanol and acetonitrile of HPLC grade were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate (~98%) and ammonium hydroxide solutions (28%~30% NH3 basis) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Milli-Q water was obtained from a Milli-Q synthesis A10 (Millipore, Bedford, MA, USA).

Instrumental analysis and quantitation

An Agilent 1290 Infinity HPLC System equipped with an Agilent 6460 Triple Quadrupole LC/MS System (Agilent Technologies, Palo Alto, CA, USA) in the negative electrospray ionization (ESI) mode was used for separation of all target analytes. The HPLC was fitted with a Aglient ZORBAX Eclipse Plus C18 (2.1×100 mm, 3.5 μm particle size) analytical column, and a suitable guard column (Agilent 1290 Infinity In-line filter with 0.3μm SS frit) was used to prevent instrument background

contamination. 2 mM ammonium acetate (A) and acetonitrile (B) were used as mobile phases. Gradient conditions were used at 0.3 mL/min flow rate and 5 µl of the sample was injected, starting with 80% A and 20% B. Initial conditions were held for 0.5 min and then decreased to 10% A at 12 min, held till 14 min, returned to initial condition at 16 min, and finally held constant until 20 min. The temperature of the column oven was kept constant at 40℃. Chromatograms were recorded using a multiple reaction monitoring mode (MRM). The following instrument parameters were used: source gas temperature (350℃), source gas flow rate (9 L/min), nebulizer pressure (40 psi), capillary (3500 V negative), delta EMV(-) (200V). The optimal settings for collision energies and declustering potential were determined for each analyte's transitions.

Quality Assurance and Quality Control (QA/QC)

All laboratory consumables and solvents were routinely checked for contamination and one procedural blank sample was conducted in every batch of seven samples. Polytetrafluoroethylene (PTFE) or other fluoropolymer materials were avoided to be used during sample collection and extraction to minimize the background contamination. Field blank, transport blank and procedure blank were prepared using Milli-Q water and routinely analyzed to check for contamination during sampling and extraction. All procedural and field blank samples were consistently below LOQ. The solvent blank was prepared using 100% methanol and run after 10 samples during instrumental analysis to minimize cross contamination and to monitor the background contamination of the instrument. Concentrations greater than the LOD in blanks were not used to correct sample concentrations in present study. Replicate experiments

including sample replicates and injection replicates were performed. Sample replicates were conducted using another same volume or amount of the sample in the same samples; and injection replicates were conducted by measuring the extract twice during instrumental analysis. Four replicates for each replicate experiment were carried out during the analysis, with RSD% less than 10%.

Instrumental drift was monitored by injecting a calibration standard (10 ng/mL) after every 10 injections and a new calibration curve was constructed if a deviation of ±20% from its initial value was observed. When the concentrations of PFAAs in any extract that was initially more than 100 ng/mL, the volume or amount of the samples would be reduced and the samples would be extracted again to fit the range of the calibration series. Matrix spike recovery tests were performed to evaluate the accuracy and precision of reported data (Loi et al., 2011), 20 ng mixtures of 12 native PFAAs standards were spiked into 400mL water samples (in small concentrations of PFAAs) via 4 duplicates, respectively. Table S3 listed detailed QA/QC measures of PFAAs in water.

Sample extraction

Water samples were extracted by OASIS WAX-SPE using a previously described method (Taniyasu et al., 2005) with minor modification and optimization. Briefly, the Oasis WAX cartridges (6 cc, 150 mg, 30 mm, Waters, Milford, MA, USA) was sequentially preconditioned with 4 mL of 0.1% NH_4OH in methanol, 4 mL methanol and 4 mL Milli-Q water. The 400-mL aliquot of water sample was spiked with 5 ng internal standard ($^{13}C_4$PFBA, $^{13}C_4$PFHxA, $^{13}C_4$PFOA, $^{13}C_4$PFNA, $^{13}C_4$PFDA,

125 $^{13}C_4$PFUdA, $^{13}C_2$PFDoA, $^{18}O_2$PFHxS and $^{13}C_4$PFOS), mixed thoroughly and then
126 loaded into the cartridges. The cartridges were washed with 4 mL of 25 mM ammonium
127 acetate (pH 4), air-dried overnight, and successively eluted with 4 mL of methanol and
128 4 mL of 0.1% NH_4OH in methanol. The eluents were collected and concentrated to 1
129 mL under a gentle stream of high-purity nitrogen (99.999%, Haidian District, Beijing,
130 China), then filtered through a nylon filter (13 mm, 0.2 mm, Chromspec, Ontario,
131 Canada) into a 1.5-mL polypropylene (PP) snap top auto-sampler vial with
132 polyethylene (PE) septa.

133 Soil samples were extracted based on published methods (Loi et al., 2011) with minor
134 modification and optimization. 2 g soil samples were placed into a 50 mL PP centrifuge
135 tube, and spiked with 10 ng mass-labelled internal standards. Sediment was digested
136 with 2 mL of 100 mM NaOH in MeOH (8:2/MeOH:Milli-Q water), and ultra-sonicated
137 for 30 min. 20 mL MeOH was added to the mixture and shaken for 30 min at 250 rpm.
138 0.1 mL of 2M HCl was added to the mixture and the sediment was separated by
139 centrifugation at 3000 rpm for 15 min. The supernatant was transferred into a new 50
140 mL tube. The extraction procedure was repeated once except that 10 mL of MeOH was
141 used instead of 20 mL. Both supernatants were combined into the same tube and
142 reduced to 1 mL under a gentle stream of high purity nitrogen. The 1 mL extracts were
143 further purified by using Supelco ENVI-Carb and Oasis WAX cartridges. The Supelco
144 ENVI-Carb cartridges (250mg, 3mL, Sigma-Aldrich, St. Louis, USA) were
145 preconditioned by passing through 1 mL MeOH three times, and then the extracts were
146 loaded and collected. Analytes were washed with another three aliquots of 1 mL MeOH

147 and collected together with the extracts. After ENVI-Carb cleanup, all the extracts were
148 diluted to 100 mL with Milli-Q water and subjected to OASIS WAX-SPE cleanup with
149 the same procedure as water samples. The final 1 mL extracts were filtered by a 13
150 mm/0.2 um nylon filter, and transferred into a 1.5 mL PP snap top brown glass vial with
151 silica septa.

152 Plant samples were extracted according to the previous methods (Felizeter et al.,
153 2012) with minor modification and optimization. 1g dry plant were placed into a 50 mL
154 PP centrifuge tube, and spiked with 10 ng mass-labelled internal standards and 6 mL
155 NaOH solution (0.4 mol/L). The tube was put in the freezer overnight after vortex. 4
156 mL TBAHS (0.5 mol/L) and 8 mL Na_2CO_3-$NaHCO_3$ buffer solution (0.25 mol/L) was
157 added successively, and then the samples were vortexed. 10 mL MTBE was added to
158 the mixture and shaken for 5 min at 700 rpm and then ultra-sonicated for 10 min. The
159 plant was separated by centrifugation at 3000 rpm for 10 min. The extraction procedure
160 was repeated once except that 5 mL of MTBE was used instead of 10 mL. Both
161 supernatants were combined into the same tube and reduced to 1 mL under a gentle
162 stream of high purity nitrogen. The 1 mL extracts were further purified by using The
163 Florisil-SEP cartridges. The Florisil-SEP cartridges were preconditioned by passing
164 through 10 mL MeOH and 10 mL MTBE. The extracts were loaded through the
165 cartridges and the tube was washed three times by MeOH. The cartridges were washed
166 with 10 mL MTBE and 10 mL MeOH-MTBE (30:70, V:V), respectively. The flow
167 velocity was kept at 1 drop per second in the whole process. The elution was reduced
168 to 1 mL under a gentle stream of high purity nitrogen. The 1 mL solution was further

purified by using Supelco ENVI-Carb cartridges. The Supelco ENVI-Carb cartridges were preconditioned by passing through 1 mL MeOH three times, and then the extracts were loaded and collected. Analytes were washed with another three aliquots of 1 mL MeOH and collected together with the extracts. All the solution in the tube was reduced to 1 mL under a gentle stream of high purity nitrogen. The final 1 mL extracts were filtered by a 13 mm/0.2 um nylon filter, and transferred into a 1.5 mL PP snap top brown glass vial with silica septa.

Detailed explanations about the calculation methods of available TDI values of PFOA

The TDI value of 1.5 μg/kg for PFOA was recommended by Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT), UK and the European Food Safety Authority (EFSA) (Benford et al., 2008; COT, 2009). The lowest no-observed-adverse-effect level (NOAELs) identified of 0.06 mg/kg per day, originated from a sub-chronic study in male rats, whereas results from long-term studies indicated higher NOAELs for effects on the liver. The Scientific Panel on Contaminants in the Food Chain (CONTAM) used modelling of the dose-response data of effects on liver from mice and male rats to calculate the lower confidence limits of the benchmark dose for a 10% effect size (BMDL10). The Panel noted that the 95% lower confidence limit of the benchmark dose for a 10% increase in effects on the liver (BMDL10) values from a number of studies in mice and male rats were in the region of 0.3 - 0.7 mg/kg b.w. per day. Therefore, the CONTAM Panel concluded that the lowest BMDL10 of 0.3 mg/kg b.w. per day was an appropriate point of departure for deriving a TDI. The

CONTAM Panel established a TDI for PFOA of 1.5 µg/kg b.w. per day by applying an overall UF of 200 to the BMDL10. An UF of 100 was used for inter- and intra-species differences and an additional UF of 2 to compensate for uncertainties relating to the internal dose kinetics. The TDI value of 1.5 µg/kg for PFOA is used to assess the potential significance of the total human exposure to PFOA.

The TDI value of 333 ng/kg for PFOA is derived from National Institute of Environmental Health Sciences (NIEHS), USA (Thayer and Houlihan, 2002). The value is a reference dose (RfD) based on a rat multigenerational study. The lowest dose tested in this study, 1 mg/kg/d, has unambiguously been interpreted as a Lowest Observed Adverse Effect Level (LOAEL). Significant changes in liver, kidney, spleen, and seminal vesicle weight were observed in adult F1 generation male rats. Again, we note that control animals in this study – as in other studies – have significant background levels of PFOA. We estimated a RfD of 0.333 µg/kg/mg for PFOA by dividing 1 mg/kg/d LOAEL by 3000. This incorporates a 10× factor to account for a lack of a NOAEL for both the reproduction and chronic toxicity/carcinogenicity studies.

The TDI value of 100 ng/kg for PFOA is recommended by German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) and the Drinking Water Commission (Trinkwasserkommission, TWK) of the German Ministry of Health at the Federal Environment Agency (BfR, 2006; TWK, 2006). According to the Draft Risk Assessment of EPA, there are several LOAELs (lowest observed adverse effect levels) and NOAELs (no observed adverse effect levels) for PFOA at various toxic end points.

A two-year study mentioned there with male and female Sprague-Dawley rats detected a LOAEL of approximately 15 mg/kg/day and a NOAEL of approximately 1.5 mg/kg/day. A LOAEL for toxicity on reproduction as measured in F0 and F1 rat generations is considered to be 1 mg/kg/day. Therefore, the lowest NOAEL for PFOA in animal studies is considered to be in the range 0.1 < 1.0 mg/kg/day. If the lower range limit is used as the point of departure (PoD) for a preliminary PFOA toxicity assessment, using an extrapolation factor4 EFcd of 10 × 10 = 100 and an additional uncertainty factor of 10 (to compensate for the extremely long half-life of PFOA in humans compared to rats), a tolerable daily intake of 0.1 µg/kg/day is obtained for all risk groups, which of course include infants and pregnant women. The TDI is the estimate of the amount of PFOA which can be ingested daily over a lifetime by a human, irrespective of his age, without any significant risk to health.

231 Table S1. Parameters measured along with rainwater samples in situ

Sites	Precipitation event	DO (mg/L)	Salinity (PSU)	CD (μs/cm)	pH
P1	Oct. 12	8.22	0.18	349	7.01
P1	Oct. 19	6.7	1.2	2152	8.75
P1	Oct. 20	8.3	0.16	318	6.86
P1	Oct. 30	7.62	0.28	538	7.88
P1	Nov. 15	7.38	0.31	593	7.37
P1	Nov. 27	8.39	0.1	198	7.06
P2	Oct. 19	8.01	0.24	465	6.5
P2	Oct. 21	7.7	0.35	643	6.44
P2	Oct. 30	7.36	0.3	582	6.55
P3	Oct. 12	7.84	0.36	679	7.36
P3	Oct. 19	7.53	0.31	570	8.31
P3	Oct. 30	8.5	0.14	267	7.73
P3	Nov. 27	8.11	0.04	82.7	6.06
P4	Oct. 20	8.59	0.2	381	7.12
P4	Oct. 30	7.92	0.16	313	7.53
P4	Nov. 27	8.69	0.02	34.9	5.51
P5	Oct. 12	8.5	0.03	51.8	6.15
P5	Oct. 19	8.52	0.05	104.2	6.33
P5	Oct. 30	8.34	0.03	35.4	5.43
P5	Nov. 15	7.62	0.14	271	5.16

232 **Note:** DO, dissolved oxygen; CD, conductivity.

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241 Table S2. Site information and ambient description

Classification	Sites	Longitude	Latitude	Ambient description
Central area within 1km from the FIP	C1	118.03128	36.96253	400m from the FIP; 170m from a village; groundwater irrigation
	C2	118.02225	36.96568	200m from the FIP; 300m from a village; groundwater irrigation
	C3	118.02155	36.97594	300m from central facility of the FIP; 300m from a village; groundwater irrigation
	C4	118.02995	36.97749	within the FIP; 150m from central facility; groundwater irrigation
	C5	118.04534	36.98298	200m from a village; 300m from a power plant; groundwater irrigation
	C6	118.04527	36.97198	200m from a village; groundwater irrigation
	C7	118.01318	36.98135	170m from a village; groundwater irrigation
	C8	118.01436	36.99742	150m from a village; groundwater irrigation
	C9(D)	118.04222	36.99164	360m from a village; irrigated by a canal from the Dongzhulong River for a long time
	C10(D)	118.03290	37.00110	200m from the Dongzhulong River and irrigated by the river for a long time
2 km from the FIP	E1	118.05902	36.97896	500m from a village; woodland and greenhouse; groundwater irrigation
	SE1	118.05511	36.96139	360m from a few residential buildings; groundwater irrigation; orchard
	S1	118.02766	36.94964	300m from a village; groundwater irrigation
	SW1	118.00440	36.96227	350m from a village; groundwater irrigation
	W1	118.00229	36.97826	Large tracts of farmland; groundwater irrigation
	NW1	118.00381	37.00189	180m from a village; groundwater irrigation
	N1(D)	118.03384	37.01217	500m from a village; 300m from the Dongzhulong River and irrigated by the river for a long time
	NE1(D)	118.05568	36.99688	300m from a village; 100m from a plastic plant; irrigated by a canal from the Dongzhulong River for a long time
4km from the FIP	E2	118.07721	36.97993	Large farmland patches; groundwater irrigation
	SE2	118.06641	36.94647	Near the county town; groundwater irrigation
	S2	118.02859	36.92846	400m from a village; groundwater irrigation
	SW2	117.98295	36.94511	250m from a village; groundwater irrigation
	W2	117.97882	36.97943	200m from a village; groundwater irrigation
	NW2	117.99043	37.01767	Large tracts of farmland; groundwater irrigation

	N2(D)	118.03446	37.03814	600m from the Dongzhulong River and irrigated by the river for a long time
	NE2	118.06859	37.01731	200m from a village; groundwater irrigation
7km from the FIP	E3	118.11406	36.98405	150m from a village; groundwater irrigation
	SE3	118.09771	36.92545	500m from the county town; groundwater irrigation; a few small workshops;
	S3	118.02836	36.90204	Large tracts of farmland; groundwater irrigation
	SW3	117.96747	36.92615	400m from a village; groundwater irrigation
	W3	117.94491	36.98299	300m from a village; groundwater irrigation
	NW3	117.96588	37.03752	400m from a village; groundwater irrigation
	N3(Y1)	118.04102	37.06661	300m from a village; 700m from the Dongzhulong River; irrigated by diverted Yellow River water
	N3(Y2)	118.04682	37.06662	500m from a village; 180m from the Dongzhulong River; irrigated by diverted Yellow River water
	NE3	118.09364	37.03454	Large tracts of farmland; groundwater irrigation
10km from the FIP	E4	118.14289	36.98178	400m from a village; groundwater irrigation
	SE4	118.12281	36.90909	350m from a village; groundwater irrigation
	S4	118.02996	36.87795	400m from a village; groundwater irrigation
	SW4	117.94326	36.90314	250m from a village; groundwater irrigation
	W4	117.92265	36.98439	500m from a village; groundwater irrigation
	NW4	117.94297	37.05457	500m from a village; groundwater irrigation
	N4(X2)	118.05234	37.10292	1000m after the confluence of the Dongzhulong River and Xiaoqing River; irrigated by the Xiaoqing River
	N4(X1)	118.03384	37.09437	1000m before the confluence of the Dongzhulong River and Xiaoqing River; irrigated by the Xiaoqing River
	NE4	118.11949	37.05190	300m from a village group; groundwater irrigation
Transverse samples from the Dongzhulong River	F1	118.03178	37.00111	300m from the river; groundwater irrigation
	F2	118.02942	37.00110	500m from the river; groundwater irrigation
	F3	118.02662	37.00115	750m from the river; groundwater irrigation
	F4	118.02384	37.00119	1000m from the river; groundwater irrigation
	F5	118.01818	37.00130	1500m from the river; groundwater irrigation

Note: D, the sites irrigated by the Dongzhulong River; X, the sites irrigated by the Xiaoqing River; Y, the sites irrigated by diverted Yellow River water.

245 Table S3. Some parameters measured in wheat soil and maize soil.

Sites	Wheat				Maize			
	pH	SOM (g/kg)	TC (%)	TN (%)	pH	SOM (g/kg)	TC (%)	TN (%)
C1	7.73	23.5	2.36	0.13	7.96	20.1	2.32	0.12
C2	7.67	17.2	1.36	0.11	7.73	18.3	1.40	0.11
C3	7.84	14.6	1.23	0.10	7.80	13.3	1.12	0.09
C4	7.83	19.5	1.46	0.11	7.96	18.3	1.42	0.11
C5	7.97	20.6	1.66	0.12	7.93	19.4	1.59	0.12
C6	8.08	18.6	1.67	0.11	8.16	19.3	1.73	0.12
C7	7.62	18.8	1.41	0.14	7.73	19.8	1.43	0.13
C8	8.19	22.4	1.62	0.13	7.96	20.3	1.67	0.13
C9(D)	7.59	18.0	1.54	0.11	7.24	25.7	2.11	0.17
C10(D)	7.87	20.4	1.69	0.12	7.87	20.0	1.75	0.12
E1	7.60	21.6	1.96	0.15	8.02	19.5	1.72	0.12
E2	8.18	23.1	1.94	0.14	8.02	19.0	1.68	0.12
E3	8.06	22.9	1.70	0.13	8.14	20.5	1.51	0.12
E4	7.69	22.3	2.23	0.14	8.31	22.9	1.92	0.14
N1(D)	7.85	12.3	1.51	0.09	8.03	25.9	2.11	0.15
N2(D)	7.49	30.0	2.62	0.17	7.90	20.0	2.39	0.13
N3(Y1)	7.99	16.1	1.72	0.10	7.75	21.2	2.06	0.12
N3(Y2)	8.02	19.2	2.02	0.12	7.75	14.1	2.05	0.08
N4(X1)	8.07	11.6	2.07	0.07	7.73	12.3	1.85	0.08
N4(X2)	8.06	16.9	2.29	0.10	7.91	13.5	1.89	0.09
NE1(D)	7.77	18.1	1.38	0.11	7.80	22.6	1.69	0.14
NE2	7.79	22.8	1.96	0.14	7.99	19.4	1.59	0.12
NE3	8.05	19.3	1.67	0.12	8.25	18.4	1.83	0.11
NE4	8.11	14.9	2.00	0.09	8.24	20.7	2.45	0.13
NW1	7.91	22.2	1.79	0.13	7.81	26.1	2.12	0.16
NW2	7.94	20.8	2.00	0.14	8.20	24.6	2.10	0.14
NW3	8.07	24.1	2.23	0.13	7.95	20.3	1.78	0.11
NW4	7.92	22.6	1.89	0.13	8.03	23.1	1.99	0.13
S1	7.57	21.5	1.63	0.13	7.33	36.0	2.58	0.20
S2	7.54	18.8	1.67	0.12	7.43	20.1	2.12	0.13
S3	7.09	21.3	1.73	0.15	7.31	14.3	1.80	0.10
S4	7.70	17.9	1.50	0.12	7.56	14.1	1.54	0.09
SE1	7.75	21.2	1.90	0.12	8.01	20.5	1.83	0.12
SE2	7.94	18.7	1.49	0.12	7.52	20.0	1.65	0.12
SE3	8.00	21.6	1.75	0.13	7.76	13.7	1.53	0.09
SE4	7.95	21.9	1.84	0.13	8.00	17.5	1.41	0.06
SW1	7.97	20.6	1.50	0.12	7.42	22.9	1.66	0.15
SW2	7.55	21.2	1.77	0.14	7.79	20.6	1.54	0.13

SW3	7.09	21.8	1.61	0.16	7.91	22.4	1.59	0.13
SW4	7.17	19.8	1.43	0.13	7.65	24.6	1.66	0.14
W1	7.88	18.9	1.55	0.12	7.85	21.6	1.57	0.14
W2	8.11	18.0	1.45	0.11	7.96	23.4	1.71	0.15
W3	8.07	22.9	1.80	0.14	8.08	24.0	2.06	0.13
W4	7.91	24.8	1.89	0.15	7.98	19.6	1.55	0.12

Note: SOM, soil organic matter; TC, total carbon; TN, total nitrogen.

260 Table S4. Target analytes and optimized MS/MS parameters used for identifying and

261 quantifying individual PFAAs

Analyte	Acronym	Carbon number	MS/MS transition	Frag (V)	CE (V)	Type of Quantification
Perfluoroalkyl carboxylic acids	**PFCAs**					
Perfluorobutanoic acid	PFBA	C4	213.0 → 169.1	57	1	$^{13}C_4$ PFBA internal
Perfluoropentanoic acid	PFPeA	C5	263.0 → 218.9	68	2	$^{13}C_4$ PFBA internal
Perfluorohexanoic acid	PFHxA	C6	313.0 → 269.0	68	3	$^{13}C_4$ PFHxA internal
			313.0 → 119.0	62	15	
Perfluoroheptanoic acid	PFHpA	C7	363.0 → 318.9	68	4	$^{13}C_4$ PFHxA internal
			363.0 → 169.0	70	9	
Perfluorooctanoic acid	PFOA	C8	413.0 → 368.9	82	4	$^{13}C_4$ PFOA internal
			413.0 → 169.0	82	12	
			413.0 → 219.0	82	10	
Perfluorononanoic acid	PFNA	C9	463.0 → 419.0	82	3	$^{13}C_4$ PFNA internal
			463.0 → 169.0	66	15	
Perfluorodecanoic acid	PFDA	C10	513.0 → 468.9	86	3	$^{13}C_4$ PFDA internal
			513.0 → 219.0	78	13	
Perfluoroundecanoic acid	PFUnDA	C11	563.0 → 519.0	90	5	$^{13}C_4$ PFUnDA internal
			563.0 → 319.0	84	15	
Perfluorododecanoic acid	PFDoDA	C12	613.0 → 569.0	90	5	$^{13}C_2$ PFDoDA internal
			613.0 → 169.0	80	23	
Perfluoroalkane sulfonic acids	**PFSAs**					
Perfluorobutane sulfonate	PFBS	C4	299.0 → 80.0	135	32	$^{18}O_2$ PFHxS internal
			299.0 → 99.0	132	24	
Perfluorohexane sulfonate	PFHxS	C6	399.0 → 80.0	150	40	$^{18}O_2$ PFHxS internal

			399.0 → 99.0	146	34	
Perfluorooctane sulfonate	PFOS	C8	498.9 → 80.0	154	47	$^{13}C_4$ PFOS internal
			498.9 → 99.0	150	42	
Internal standards						
$^{13}C_4$ Perfluorobutanoic acid	$^{13}C_4$ PFBA	-	217.0 → 172.0	57	1	-
$^{13}C_4$ Perfluorohexanoic acid	$^{13}C_4$ PFHxA	-	315.0 → 270.0	68	3	-
$^{13}C_4$ Perfluorooctanoic acid	$^{13}C_4$ PFOA	-	417.0 → 372.0	82	4	-
$^{13}C_4$ Perfluorononanoic acid	$^{13}C_4$ PFNA	-	468.0 → 423.0	82	3	-
$^{13}C_4$ Perfluorodecanoic acid	$^{13}C_4$ PFDA	-	515.0 → 470.0	86	3	-
$^{13}C_4$ Perfluoroundecanoic acid	$^{13}C_4$ PFUnDA	-	565.0 → 520.0	90	5	-
$^{13}C_2$ Perfluorododecanoic acid	$^{13}C_2$ PFDoDA	-	615.0 → 570.0	90	5	-
$^{18}O_2$ Perfluorohexane sulfonate	$^{18}O_2$ PFHxS	-	403.0 → 103.0	150	40	-
$^{13}C_4$ Perfluorooctane sulfonate	$^{13}C_4$ PFOS	-	503.0 → 99.0	154	47	-

Note: The terminology used in this study was based on (Buck et al., 2011); Frag, fragment voltage; CE, collision energy.

277 Table S5. Analyses of 12 PFASs measured in the study with QA/QC information

Analytes	Rain water/(ng/L)				Soil/(ng/g)				Plant/(ng/g)			
	LOD	LOQ	MSR (%)	DF (%)	LOD	LOQ	MSR (%)	DF (%)	LOD	LOQ	MSR (%)	DF (%)
PFCAs												
PFBA	0.08	0.22	109	100	0.01	0.04	73.3	98.9	0.1	0.5	81.2	100
PFPeA	0.05	0.15	88.2	100	0.01	0.03	72.5	98.9	0.05	0.15	66.4	95.5
PFHxA	0.04	0.15	90.1	100	0.004	0.01	79.4	100	0.02	0.07	77.7	100
PFHpA	0.06	0.15	79.0	100	0.006	0.02	75.8	100	0.03	0.1	102	65.9
PFOA	0.05	0.19	104	100	0.002	0.01	72.4	100	0.01	0.05	78.9	100
PFNA	0.06	0.13	87.4	100	0.002	0.01	80.0	100	0.01	0.05	75.5	81.8
PFDA	0.05	0.15	100	100	0.004	0.01	75.2	100	0.02	0.07	78.2	67.1
PFUnDA	0.03	0.08	97.8	65	0.008	0.02	77.4	85.2	0.04	0.1	73.2	34.1
PFDoDA	0.05	0.13	88.8	40	0.005	0.02	83.2	58.0	0.02	0.06	78.4	38.6
PFSAs												
PFBS	0.03	0.09	83.5	35	0.004	0.01	93.0	5.68	0.02	0.05	81.4	18.2
PFHxS	0.01	0.06	83.5	75	0.004	0.01	79.7	3.41	0.02	0.04	81.8	5.68
PFOS	0.03	0.10	92.2	75	0.004	0.01	85.3	87.5	0.02	0.05	78.6	65.9

278 **Note:** LOD, the limit of detection; LOQ, the limit of quantification; MSR, matrix spike
279 recoveries; DF, detection frequencies.

280 Table S6. Parameters used for calculation of daily intake of PFAAs by infants, toddlers,
281 children, teenagers and adults via consumption of wheat and maize grain in this study
282 (Bureau of Statistics of Shandong Province, China, 2015; Zhai, 2008; Yang et al., 2005;
283 Zhang et al., 2010).

	DC_{wheat} (g/d)	DC_{maize} (g/d)	BW (kg)
Toddlers (2-5 yrs)	123	11.8	16.5
Children (6-10 yrs)	216	20.7	28.6
Teenagers (11-17 yrs)	277	26.6	48.3
Adults (≥18 yrs)	308	30.0	60.5

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285 Table S7. Concentrations of PFAAs (ng/g) in wheat soil.

sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	∑PFAAs
C1	1.04	0.70	0.59	0.96	59.5	0.09	0.07	0.04	<0.02	<0.01	<0.01	0.10	63.2
C2	0.12	0.64	0.45	0.60	69.0	0.11	0.27	0.07	0.12	<0.01	<0.01	<0.01	71.4
C3	4.76	2.86	1.53	0.71	83.2	0.04	0.06	<0.02	0.04	<0.01	<0.01	0.14	93.3
C4	3.69	4.08	4.04	4.51	380.6	0.23	0.19	0.06	0.03	0.02	<0.01	4.27	402
C5	0.96	0.70	0.61	0.34	16.3	0.02	0.08	0.07	<0.02	<0.01	<0.01	0.18	19.3
C6	1.18	0.70	0.51	0.24	15.7	0.06	0.06	0.05	<0.02	<0.01	<0.01	0.07	18.6
C7	2.31	2.01	1.10	0.28	21.7	0.04	0.06	0.20	<0.02	<0.01	<0.01	<0.01	27.7
C8	0.42	0.36	0.34	0.08	10.7	0.07	0.03	<0.02	0.02	<0.01	<0.01	1.97	14.1
C9(D)	2.68	3.69	4.72	5.83	623	0.48	0.14	0.04	<0.02	<0.01	<0.01	0.10	641
C10(D)	3.08	3.67	3.10	2.11	242	0.11	0.08	0.02	0.03	<0.01	<0.01	0.24	254
E1	0.89	0.46	0.35	0.16	10.1	0.16	0.05	0.06	0.03	<0.01	<0.01	0.13	12.4
E2	0.45	0.32	0.19	0.09	5.81	0.05	0.03	0.06	<0.02	<0.01	<0.01	0.05	7.07
E3	0.37	0.22	0.07	0.04	4.53	0.05	0.06	0.02	<0.02	<0.01	<0.01	0.03	5.40
E4	0.22	0.07	0.09	<0.02	2.95	0.01	<0.01	<0.02	0.02	0.05	<0.01	0.08	3.51
N1(D)	3.23	4.86	4.74	2.35	498	0.23	0.06	0.03	0.02	<0.01	<0.01	0.15	513
N2(D)	1.99	3.11	4.46	2.13	291	0.18	0.10	0.07	0.04	<0.01	<0.01	0.39	304
N3(Y1)	0.51	0.42	0.52	0.26	46.9	0.04	0.05	<0.02	0.04	<0.01	<0.01	0.18	48.9
N3(Y2)	0.61	0.54	0.51	0.36	123.6	0.20	0.06	0.03	<0.02	<0.01	<0.01	0.13	126
N4(X1)	0.09	<0.03	0.10	0.04	2.17	0.15	0.13	0.10	0.05	<0.01	<0.01	0.09	2.94
N4(X2)	0.21	0.50	0.93	0.69	32.1	0.42	1.30	0.48	0.23	<0.01	<0.01	0.61	37.4
NE1(D)	2.93	4.53	4.25	2.15	217	0.07	0.07	0.02	<0.02	<0.01	<0.01	0.05	231
NE2	0.84	0.55	0.57	0.22	15.1	0.09	0.08	0.07	0.05	<0.01	<0.01	0.17	17.7
NE3	0.52	0.45	0.41	0.20	12.4	0.05	0.05	0.03	0.03	<0.01	<0.01	0.13	14.3

NE4	0.42	0.20	0.34	0.09	6.85	0.03	0.03	0.03	<0.02	<0.01	<0.01	0.07	8.09
NW1	0.26	0.24	0.26	0.08	7.36	0.05	0.05	0.03	<0.02	<0.01	<0.01	0.06	8.40
NW2	0.24	0.17	0.18	0.11	4.25	0.04	<0.01	<0.02	<0.02	<0.01	<0.01	0.04	5.06
NW3	0.28	0.04	0.25	0.05	3.99	0.08	0.06	0.08	0.05	<0.01	<0.01	0.05	4.93
NW4	0.12	0.14	0.14	<0.02	3.71	0.06	0.03	0.03	0.03	<0.01	<0.01	0.10	4.37
S1	0.74	0.48	0.59	0.30	25.3	0.07	0.12	0.03	0.13	<0.01	<0.01	0.20	28.0
S2	0.61	0.43	0.39	0.11	7.44	0.08	0.06	0.04	0.09	<0.01	<0.01	0.15	9.41
S3	0.44	0.16	0.21	0.06	5.08	0.02	0.03	0.03	<0.02	<0.01	<0.01	0.03	6.08
S4	0.29	0.05	0.13	0.06	2.51	0.01	0.05	<0.02	<0.02	<0.01	<0.01	0.03	3.15
SE1	1.00	0.99	0.70	0.23	16.4	0.06	0.09	0.03	0.08	<0.01	<0.01	0.03	19.6
SE2	0.38	0.18	0.20	0.03	5.86	0.07	0.06	0.07	0.03	<0.01	<0.01	<0.01	6.88
SE3	0.43	0.31	0.20	0.26	10.9	0.07	0.06	0.03	0.03	<0.01	<0.01	0.07	12.4
SE4	0.26	0.03	0.07	<0.02	3.54	0.02	0.03	0.04	0.02	<0.01	<0.01	0.11	4.14
SW1	0.59	0.64	0.46	0.17	14.5	0.05	0.09	0.02	<0.02	<0.01	<0.01	0.03	16.5
SW2	0.52	0.29	0.21	0.16	9.86	0.06	0.06	<0.02	<0.02	<0.01	<0.01	0.02	11.2
SW3	0.25	0.11	0.14	0.06	6.07	0.10	0.05	0.05	0.02	<0.01	<0.01	0.08	6.93
SW4	0.27	0.18	0.16	0.06	4.45	0.07	0.07	0.03	<0.02	<0.01	<0.01	<0.01	5.31
W1	0.60	0.59	0.33	0.13	13.8	0.07	0.08	<0.02	<0.02	<0.01	<0.01	0.09	15.7
W2	0.48	0.42	0.35	0.09	16.0	0.03	0.07	0.04	<0.02	<0.01	<0.01	0.46	18.0
W3	0.47	0.42	0.37	0.13	11.3	0.02	0.10	<0.02	0.04	<0.01	<0.01	0.04	12.9
W4	0.19	0.27	0.14	0.05	5.12	0.04	0.07	<0.02	0.02	<0.01	<0.01	0.10	6.02

Note: "<" means the value below LOQ (the same below).

288 Table S8. Concentrations of PFAAs (ng/g) in maize soil.

sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	∑PFAAs
C1	0.85	0.79	0.51	0.62	65.0	0.13	0.11	0.04	<0.02	<0.01	<0.01	0.02	68.1
C2	2.36	1.54	0.90	1.12	78.7	0.19	0.09	0.05	<0.02	<0.01	<0.01	0.17	85.1
C3	4.55	2.53	1.39	1.53	92.8	0.13	0.10	0.05	0.03	<0.01	<0.01	0.07	103
C4	3.12	4.04	2.46	1.84	341	0.33	0.13	0.02	<0.02	<0.01	0.05	35.5	388
C5	1.90	1.28	1.04	0.65	22.9	0.01	0.11	0.03	<0.02	<0.01	<0.01	<0.01	27.9
C6	1.13	0.73	0.55	0.26	15.6	0.04	0.10	<0.02	<0.02	<0.01	<0.01	<0.01	18.4
C7	1.44	1.09	0.84	0.48	24.3	0.07	0.07	<0.02	<0.02	<0.01	<0.01	0.07	28.4
C8	0.43	0.32	0.23	0.13	7.51	0.05	0.08	0.03	<0.02	<0.01	<0.01	0.19	8.97
C9(D)	2.50	1.67	1.83	1.17	294	0.33	0.17	0.06	<0.02	<0.01	<0.01	0.18	302
C10(D)	3.07	3.01	2.49	1.31	214	0.18	0.07	<0.02	<0.02	<0.01	<0.01	0.43	224
E1	1.22	0.82	0.98	0.38	26.4	0.07	0.05	0.03	<0.02	<0.01	<0.01	0.06	30.0
E2	0.72	0.49	0.41	0.17	7.45	0.02	0.02	<0.02	<0.02	<0.01	<0.01	0.02	9.32
E3	0.40	0.22	0.19	0.08	3.61	0.04	0.03	0.02	<0.02	<0.01	<0.01	<0.01	4.60
E4	0.36	0.19	0.13	0.11	3.78	0.03	0.03	<0.02	<0.02	0.04	<0.01	0.03	4.72
N1(D)	2.07	3.16	3.94	2.81	608	0.42	0.25	0.01	<0.02	<0.01	<0.01	7.03	627
N2(D)	0.77	1.05	1.10	0.59	108	0.09	0.13	0.03	<0.02	<0.01	<0.01	0.59	112
N3(Y1)	0.38	0.18	0.43	0.17	25.5	0.05	0.06	<0.02	<0.02	<0.01	<0.01	2.68	29.4
N3(Y2)	2.06	0.74	1.21	0.39	49.0	0.05	0.20	0.08	<0.02	<0.01	<0.01	1.01	54.8
N4(X1)	0.19	0.09	0.14	0.16	2.46	0.17	0.52	0.16	0.12	<0.01	<0.01	0.10	4.11
N4(X2)	0.44	0.43	0.87	0.38	53.0	0.10	0.12	0.06	<0.02	<0.01	<0.01	0.11	55.6
NE1(D)	2.48	2.71	2.04	1.32	260	0.30	0.15	<0.02	<0.02	<0.01	<0.01	0.14	269
NE2	0.73	0.43	0.40	0.25	12.8	0.08	0.08	0.09	<0.02	<0.01	<0.01	0.15	15.1
NE3	0.92	0.51	0.37	0.23	13.0	0.04	0.05	<0.02	<0.02	<0.01	<0.01	0.02	15.2

NE4	0.43	0.29	0.30	0.14	8.27	0.04	0.06	0.05	<0.02	<0.01	<0.01	0.08	9.67
NW1	0.43	0.30	0.28	0.17	7.94	0.02	0.01	0.04	<0.02	<0.01	<0.01	<0.01	9.20
NW2	0.48	0.18	0.14	0.09	5.49	0.08	0.03	<0.02	<0.02	<0.01	<0.01	0.06	6.57
NW3	0.36	0.21	0.28	0.08	5.02	0.04	0.04	0.02	<0.02	<0.01	<0.01	0.30	6.38
NW4	0.21	0.09	0.15	0.07	3.20	0.01	0.05	<0.02	<0.02	<0.01	<0.01	0.02	3.81
S1	0.32	0.23	0.19	0.10	10.5	0.07	0.06	0.07	<0.02	<0.01	<0.01	0.20	11.7
S2	0.41	0.31	0.34	0.12	7.58	0.09	0.12	<0.02	<0.02	<0.01	0.02	0.47	9.46
S3	0.20	0.09	0.16	0.09	4.37	0.04	0.09	0.02	<0.02	<0.01	<0.01	0.18	5.24
S4	0.27	0.11	0.17	0.03	2.41	0.05	0.05	0.03	<0.02	<0.01	<0.01	0.08	3.20
SE1	0.93	0.66	0.35	0.24	11.4	0.05	0.03	<0.02	0.03	<0.01	<0.01	<0.01	13.7
SE2	0.24	0.13	0.21	0.05	3.13	0.01	0.05	<0.02	<0.02	<0.01	<0.01	<0.01	3.84
SE3	0.29	0.16	0.15	0.07	3.45	0.04	0.03	<0.02	<0.02	<0.01	<0.01	0.07	4.28
SE4	0.21	0.07	0.11	0.05	1.29	0.06	0.02	<0.02	<0.02	<0.01	<0.01	0.04	1.86
SW1	1.01	0.70	0.51	0.30	22.8	0.06	0.08	<0.02	<0.02	<0.01	<0.01	0.05	25.5
SW2	0.46	0.23	0.15	0.12	6.62	0.04	0.05	0.02	<0.02	<0.01	<0.01	0.05	7.75
SW3	0.38	0.21	0.10	0.10	5.70	0.05	0.04	<0.02	<0.02	<0.01	<0.01	0.08	6.68
SW4	0.01	0.12	0.08	0.08	2.82	0.06	0.04	<0.02	<0.02	<0.01	<0.01	<0.01	3.23
W1	1.04	0.76	0.57	0.32	20.6	0.10	0.11	0.04	<0.02	<0.01	<0.01	0.09	23.7
W2	0.75	0.53	0.49	0.17	12.8	0.07	0.04	0.03	<0.02	<0.01	<0.01	0.05	14.9
W3	0.35	0.34	0.14	0.08	7.42	0.05	0.07	<0.02	<0.02	<0.01	<0.01	0.02	8.49
W4	0.18	0.13	0.09	0.09	3.75	0.04	0.07	<0.02	<0.02	<0.01	<0.01	0.03	4.39

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290 Table S9. PFOS/PFOA concentrations (ng/g) in soil previously reported in China.

Regions	Cities	PFOS	PFOA	∑PFAAs	Ref [b]
Northeast China	Dandong	nd	nd	0.30 [a]	(1)
	Dalian	nd	nd	0.12 [a]	(1)
	Yingkou	0.26 [a]	0.08 [a]	1.10 [a]	(1)
	Panjin	nd	0.05 [a]	0.23 [a]	(1)
	Jinzhou	0.01 [a]	0.21 [a]	0.63 [a]	(1)
	Huludao	0.11 [a]	0.20 [a]	0.74 [a]	(1)
North China	Guanting Reservoir	nd-0.86	nd-2.8	0.13-8.50	(2)
	Beijing	0.40 [a]	0.30 [a]	-	(3)
	Tianjin Binhai area	1.88 [a]	0.41 [a]	3.55 [a]	(1)
	Qinhuangdao	0.09 [a]	nd	0.30 [a]	(1)
	Tangshan	nd	nd	0.04 [a]	(1)
East China	Dezhou	0.15 [a]	0.25 [a]	0.55 [a]	(1)
	Binzhou	0.11 [a]	0.58 [a]	0.91 [a]	(1)
	Dongying	0.10 [a]	2.32 [a]	2.60 [a]	(1)
	Weifang	0.12 [a]	0.33 [a]	0.59 [a]	(1)
	Yantai	0.13 [a]	0.14 [a]	0.42 [a]	(1)
	Weihai	0.11 [a]	0.06 [a]	0.31 [a]	(1)
	Qingdao	0.17 [a]	0.26 [a]	0.73 [a]	(1)
	Shanghai	8.58-10.4	3.28-47.5	141-237	(4)
Central China	Huaihe Watershed	nd-0.21	nd-0.2	nd-1.22	(5)
South China	Guangzhou	0.05-0.83	0.02-0.09	0.09-1.02	(3)
	Dongguan	0.12-1.48	0.05-0.48	0.19-1.96	(3)
	Shenzhen	0.07-2.41	0.03-0.53	0.11-2.58	(3)
	Zhuhai	0.05-1.21	0.03-1.24	0.09-2.45	(3)

291 **Note:** a, the average concentration; b, references: (1) Meng et al. (2015); (2) Wang et

292 al. (2011); (3) Guo-Cheng et al. (2013); (4) Li et al. (2010); (5) Meng et al. (2013).

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297 Table S10 Concentration relationship of PFAAs in irrigation water and soil (n=30)

Component	Carbon chain length	Equations	R^2	p
PFBA	4	$Log_{10}C_{soil} = 0.19 \times Log_{10}C_{irrigation} - 0.48$	0.60	<0.01
PFPeA	5	$Log_{10}C_{soil} = 0.21 \times Log_{10}C_{irrigation} - 0.61$	0.60	<0.01
PFHxA	6	$Log_{10}C_{soil} = 0.22 \times Log_{10}C_{irrigation} - 0.64$	0.71	<0.01
PFHpA	7	$Log_{10}C_{soil} = 0.26 \times Log_{10}C_{irrigation} - 0.89$	0.77	<0.01
PFOA	8	$Log_{10}C_{soil} = 0.30 \times Log_{10}C_{irrigation} + 0.51$	0.81	<0.01
∑PFAAs		$Log_{10}C_{soil} = 0.30 \times Log_{10}C_{irrigation} + 0.50$	0.82	<0.01

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299 Table S11. Concentrations of PFAAs (ng/L) in rainwater.

sites	Precipitation event	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	∑PFAAs
P1	Oct. 12	447	111	81.2	130	1451	4.62	3.58	0.67	0.14	<0.09	<0.06	<0.1	2229
P1	Oct. 19	227	260	554	944	2627	9.79	7.39	0.62	<0.13	<0.09	0.67	0.78	4631
P1	Oct. 20	85.9	30.1	25.7	54.6	1432	2.45	2.25	0.26	<0.13	<0.09	<0.06	0.71	1634
P1	Oct. 30	97.9	42.0	37.8	120	1358	4.10	3.50	0.60	0.18	1.21	0.15	0.51	1666
P1	Nov. 15	804	420	376	498	2752	4.96	4.28	1.58	0.39	<0.09	0.10	0.44	4862
P1	Nov. 27	10.1	4.93	3.55	3.58	53.7	0.15	0.18	<0.08	<0.13	<0.09	0.12	<0.1	76.4
P2	Oct. 19	94.5	29.8	57.4	175	1285	1.56	1.18	0.09	<0.13	0.31	0.83	0.93	1646
P2	Oct. 21	3.90	52.2	41.3	91.8	713	1.68	0.63	0.09	<0.13	1.33	4.46	0.57	911
P2	Oct. 30	91.5	28.9	51.6	146	844	3.79	0.25	<0.08	<0.13	0.17	1.26	0.55	1168
P3	Oct. 12	66.8	26.5	32.4	47.2	666	5.41	1.51	<0.08	<0.13	<0.09	0.07	0.29	846
P3	Oct. 19	7.84	4.73	4.01	5.47	176	0.39	0.41	<0.08	<0.13	<0.09	<0.06	<0.1	199
P3	Oct. 30	9.96	4.42	4.59	4.38	61.0	0.48	0.26	<0.08	<0.13	<0.09	<0.06	<0.1	85.2
P3	Nov. 27	13.4	4.79	3.88	4.82	102	0.14	0.28	<0.08	<0.13	<0.09	<0.06	<0.1	129
P4	Oct. 20	122	71.6	57.9	40.3	1065	1.44	1.33	0.09	<0.13	<0.09	0.11	0.41	1360
P4	Oct. 30	58.9	32.5	35.6	64.4	564	1.31	1.05	0.29	<0.13	0.32	<0.06	0.45	759
P4	Nov. 27	6.94	3.21	2.41	2.03	44.7	0.14	<0.15	<0.08	<0.13	<0.09	<0.06	<0.1	59.6
P5	Oct. 12	10.1	4.56	4.28	5.31	101	1.27	0.32	<0.08	<0.13	<0.09	0.08	0.21	127
P5	Oct. 19	9.76	3.91	2.96	3.11	223	<0.13	<0.15	<0.08	<0.13	<0.09	<0.06	<0.1	243
P5	Oct. 30	5.40	2.84	2.57	3.72	45.0	0.31	0.03	<0.08	<0.13	<0.09	<0.06	<0.1	60.0
P5	Nov. 15	30.4	6.57	4.66	5.73	164	0.46	0.21	0.10	<0.13	<0.09	0.10	1.35	213

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301 Table S12. Comparison of PFOS/PFOA concentrations (ng/L) in precipitation from

302 available studies by other groups.

Country	Region	PFOS	PFOA	∑PFAAs	Precipitation type	Sampling location	Ref[f]
China	Hong Kong	nd-0.7	0.2-0.41	11.2[b]	Rain	Urban	(1)
	Shenyang	nd-51	0.82-13	-	Snow	Urban	(2)
	Dalian	26.9-545	8.08-65.8	-	Snow	Urban	(3)
		9.92-113	32.9-40.8	-	Rain	Urban	(3)
	Weifang	-	-	152[a, b]	Rain	Urban	(4)
	Changchun	-	-	92.6[b]	Rain	Urban	(4)
	Beijing	15.4[b]	30.9[b]	105[b]	Snow	Urban	(5)
	Tianjin	33[b]	107[b]	229[b]	Snow	Urban	(5)
USA	Albany,NY	nd-1.93	nd-19.6	0.91-23.9	Snow	Urban	(6)
		nd-1.51	nd-7.27	0.91-13.2	Rain	Urban	(6)
		nd-0.29	0.26-9.42	15.5[b]	Rain	Urban[c]	(1)
	Slingerlands	nd-0.64	0.25-3.3	9.82[b]	Rain	Urban[d]	(1)
Japan	Yokohama	0.16[b]	95.3[b]	-	Snow	Urban	(7)
		0.12[b]	1.55[b]	-	Rain	Urban	(7)
	Tsukuba	nd-1.34	0.11-11	18.1[b]	Rain	Urban[d]	(1)
	Kawaguchi	nd-4.21	0.23-8.84	14.0[b]	Rain	Urban[e]	(1)
Germany	Northern region	0.1-3.3	0-9.3	0.8-45.5	Rain	Rural	(8)
France	Toulouse	nd-0.23	0.21	3.22[b]	Rain	Urban	(1)
India	Patna	nd-0.08	0.05-0.43	1.40[b]	Rain	Urban	(1)

303 **Note:** a, concentration of ∑PFAAs dominated by PFOA; b, the average concentration;

304 c, sampling sites are located in business area; d, sampling sites are located in residential

305 area; e, sampling sites are located in industrial area; f, references:(1) Kwok et al. (2010);

306 (2) Liu et al. (2009a); (3) Liu et al. (2009b); (4) Zhao et al. (2013); (5) Shan et al. (2015);

307 (6) Kim and Kannan (2007); (7) Salam et al. (2009); (8) Dreyer et al. (2010).

308 Table S13. Concentrations of PFAAs (ng/g) in wheat grain.

sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	∑PFAAs
C1	68.7	9.24	1.68	1.02	4.42	0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	85.1
C2	0.79	24.7	7.58	0.70	2.49	0.06	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	36.3
C3	342	47.1	9.21	1.25	6.68	0.09	0.08	0.11	<0.06	<0.05	0.05	0.18	406
C4	256	55.6	23.6	5.75	39.3	0.13	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	380
C5	56.8	9.45	2.38	1.46	4.10	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	74.1
C6	137	30.5	2.03	0.59	3.58	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	174
C7	75.1	11.6	4.47	0.94	3.78	0.09	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	95.9
C8	5.98	0.97	0.20	0.18	1.11	<0.05	<0.07	<0.1	0.07	<0.05	<0.04	0.28	8.79
C9(D)	260	54.0	39.6	3.83	12.4	0.06	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	370
C10(D)	202	35.7	10.3	1.18	9.71	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	259
E1	7.00	1.71	0.78	0.36	3.15	0.05	<0.07	<0.1	<0.06	0.06	<0.04	<0.05	13.1
E2	5.79	1.53	0.99	0.23	2.32	0.07	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	10.9
E3	5.96	1.32	0.04	0.12	1.92	0.06	0.09	<0.1	<0.06	0.09	<0.04	0.08	9.68
E4	2.78	0.73	0.45	<0.1	0.85	0.07	<0.07	<0.1	<0.06	<0.05	<0.04	0.05	4.94
N1(D)	339	83.2	49.0	2.06	6.79	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	480
N2(D)	66.2	13.1	6.37	0.58	2.37	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.15	88.7
N3(Y1)	37.3	9.96	3.61	0.50	2.87	0.05	<0.07	<0.1	<0.06	0.05	<0.04	<0.05	54.3
N3(Y2)	111	18.8	3.26	1.12	5.24	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.06	140
N4(X1)	0.39	<0.15	0.20	<0.1	0.39	0.08	<0.07	<0.1	<0.06	<0.05	<0.04	0.07	1.13
N4(X2)	7.84	5.99	5.78	0.78	2.55	0.63	0.13	0.15	0.17	<0.05	<0.04	0.21	24.2
NE1(D)	123	24.7	10.1	0.63	2.58	0.13	0.07	0.13	<0.06	<0.05	0.08	0.12	162
NE2	22.2	9.03	2.86	0.11	1.44	0.08	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	35.8
NE3	16.9	3.92	0.84	<0.1	0.58	0.06	<0.07	<0.1	<0.06	<0.05	<0.04	0.05	22.3

NE4	5.35	1.32	0.41	0.10	0.72	<0.05	<0.07	<0.1	<0.06	0.09	<0.04	0.07	8.06
NW1	2.38	0.85	0.14	<0.1	0.56	0.05	0.06	<0.1	<0.06	<0.05	<0.04	0.07	4.11
NW2	0.82	0.44	0.09	<0.1	0.28	0.07	<0.07	<0.1	<0.06	<0.05	0.04	0.07	1.80
NW3	0.78	0.17	0.12	0.12	0.25	0.20	<0.07	0.25	<0.06	0.05	<0.04	0.86	2.79
NW4	0.65	<0.15	<0.07	<0.1	0.30	0.20	<0.07	0.15	<0.06	<0.05	<0.04	0.29	1.59
S1	11.4	1.82	1.14	0.29	1.74	0.07	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	16.4
S2	9.56	1.36	0.76	<0.1	0.89	0.11	<0.07	<0.1	0.06	<0.05	<0.04	<0.05	12.7
S3	1.88	0.36	0.16	<0.1	0.56	0.07	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	3.02
S4	0.78	<0.15	<0.07	<0.1	0.61	0.11	0.09	<0.1	<0.06	<0.05	<0.04	0.06	1.65
SE1	11.7	3.62	1.55	0.35	3.09	0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	20.4
SE2	2.22	0.36	0.12	0.11	0.41	0.06	0.11	<0.1	0.08	<0.05	<0.04	0.11	3.58
SE3	2.10	0.55	0.13	0.15	0.58	<0.05	0.09	<0.1	0.06	<0.05	<0.04	<0.05	3.65
SE4	0.84	0.24	0.17	<0.1	0.52	0.07	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.84
SW1	20.0	3.23	1.15	0.26	2.35	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	27.0
SW2	8.29	1.40	0.48	<0.1	0.68	0.11	<0.07	<0.1	<0.06	<0.05	<0.04	0.80	11.8
SW3	0.91	<0.15	0.09	<0.1	0.31	<0.05	<0.07	<0.1	0.07	<0.05	<0.04	0.09	1.45
SW4	0.96	<0.15	0.10	<0.1	0.34	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.07	1.47
W1	12.9	2.89	1.51	<0.1	3.10	<0.05	0.09	<0.1	<0.06	<0.05	<0.04	0.09	20.5
W2	8.27	1.73	0.39	0.23	1.01	0.09	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	11.8
W3	2.30	0.59	0.13	<0.1	0.70	0.07	<0.07	<0.1	<0.06	<0.05	<0.04	0.14	3.92
W4	3.40	0.95	0.29	0.23	1.39	0.05	<0.07	<0.1	<0.06	<0.05	0.07	0.09	6.48

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311 Table S14. Concentrations of PFAAs (ng/g) in maize grain.

sites	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS	∑PFAAs
C1	6.31	1.26	1.48	<0.1	0.17	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	9.36
C2	2.44	0.36	2.24	<0.1	0.16	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	5.37
C3	37.37	7.65	13.04	<0.1	0.40	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.23	58.8
C4	8.69	1.44	2.19	0.07	0.17	0.02	<0.07	<0.1	<0.06	0.02	<0.04	0.04	12.7
C5	5.84	1.58	3.54	<0.1	0.31	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	11.4
C6	7.65	2.76	3.06	<0.1	0.32	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	14.0
C7	0.79	0.20	0.47	<0.1	0.16	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.79
C8	2.13	0.73	0.95	0.14	0.07	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	4.13
C9(D)	6.79	0.33	1.39	<0.1	0.24	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.14	9.04
C10(D)	34.63	3.28	3.54	1.02	0.70	<0.05	0.07	<0.1	<0.06	0.08	<0.04	<0.05	43.4
E1	1.39	0.36	0.78	<0.1	0.13	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	2.90
E2	0.83	0.40	1.03	<0.1	0.13	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	2.55
E3	0.96	0.24	0.89	<0.1	0.12	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	2.35
E4	0.60	0.53	0.99	<0.1	0.07	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	2.32
N1(D)	2.33	0.49	2.27	0.20	0.14	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	5.59
N2(D)	1.07	0.75	0.33	0.12	0.15	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.21	2.77
N3(Y1)	0.90	0.16	0.49	0.16	0.11	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.96
N3(Y2)	2.31	0.50	0.37	<0.1	0.14	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	3.52
N4(X1)	<0.5	<0.15	0.13	<0.1	0.11	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.05	0.78
N4(X2)	<0.5	0.19	0.30	<0.1	0.15	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.13	1.23
NE1(D)	6.78	0.24	0.92	<0.1	0.26	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	8.34
NE2	0.54	0.36	0.31	<0.1	0.10	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	1.55
NE3	0.68	<0.15	0.26	<0.1	0.09	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.28

NE4	<0.5	<0.15	0.43	<0.1	0.14	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.06	1.09
NW1	1.00	<0.15	0.42	0.12	0.16	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	1.99
NW2	0.72	0.23	0.46	<0.1	0.12	<0.05	<0.07	<0.1	0.10	0.07	<0.04	<0.05	1.85
NW3	0.75	0.17	0.39	<0.1	0.06	0.09	<0.07	<0.1	<0.06	<0.05	<0.04	0.09	1.71
NW4	<0.5	<0.15	0.14	0.18	<0.05	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.06	0.83
S1	<0.5	<0.15	0.52	<0.1	0.13	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.13
S2	<0.5	<0.15	0.48	<0.1	0.14	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.09
S3	<0.5	<0.15	0.21	<0.1	0.11	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	0.79
S4	<0.5	<0.15	0.14	<0.1	0.05	<0.05	0.10	<0.1	<0.06	<0.05	<0.04	0.09	0.84
SE1	4.15	1.48	1.40	0.64	0.19	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	7.99
SE2	0.50	0.65	1.21	<0.1	0.12	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.07	2.71
SE3	0.56	0.15	0.45	<0.1	0.09	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	1.46
SE4	<0.5	<0.15	0.16	<0.1	0.09	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	0.70
SW1	3.40	0.86	1.52	<0.1	0.31	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.11	6.34
SW2	1.85	0.31	0.97	0.20	0.11	0.45	0.09	0.60	<0.06	<0.05	<0.04	0.69	5.33
SW3	0.58	<0.15	0.12	<0.1	0.12	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.07	1.11
SW4	<0.5	<0.15	0.16	<0.1	0.09	0.17	<0.07	0.22	<0.06	<0.05	<0.04	0.10	1.18
W1	1.98	0.73	1.13	<0.1	0.12	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.11	4.25
W2	3.78	0.51	0.98	<0.1	0.14	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	0.10	5.67
W3	0.56	0.21	0.63	0.24	0.16	<0.05	<0.07	0.21	<0.06	<0.05	<0.04	0.07	2.21
W4	<0.5	<0.15	0.22	<0.1	0.14	<0.05	<0.07	<0.1	<0.06	<0.05	<0.04	<0.05	0.83

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Table S15. Bioaccumulation equations of PFAAs in wheat and maize grain (n=44)

	Component	Carbon chain length	Bioaccumulation equations	R^2	p
Wheat	PFBA	4	$Log_{10}C_{grain} = 1.84 \times Log_{10}C_{soil} + 1.43$	0.82	<0.01
	PFPeA	5	$Log_{10}C_{grain} = 1.31 \times Log_{10}C_{soil} + 0.85$	0.78	<0.01
	PFHxA	6	$Log_{10}C_{grain} = 1.48 \times Log_{10}C_{soil} + 0.47$	0.78	<0.01
	PFHpA	7	$Log_{10}C_{grain} = 0.73 \times Log_{10}C_{soil} - 0.14$	0.62	<0.01
	PFOA	8	$Log_{10}C_{grain} = 0.61 \times Log_{10}C_{soil} - 0.57$	0.66	<0.01
	∑PFAAs		$Log_{10}C_{grain} = 1.06 \times Log_{10}C_{soil} - 0.14$	0.81	<0.01
Maize	PFBA	4	$Log_{10}C_{grain} = 1.30 \times Log_{10}C_{soil} + 0.32$	0.72	<0.01
	PFPeA	5	$Log_{10}C_{grain} = 0.84 \times Log_{10}C_{soil} - 0.24$	0.50	<0.01
	PFHxA	6	$Log_{10}C_{grain} = 0.65 \times Log_{10}C_{soil} + 0.08$	0.40	<0.01
	PFOA	8	$Log_{10}C_{grain} = 0.22 \times Log_{10}C_{soil} - 1.14$	0.37	<0.01
	∑PFAAs		$Log_{10}C_{grain} = 0.50 \times Log_{10}C_{soil} - 0.17$	0.48	<0.01

323 Table S16. Estimated Daily Intake (EDI, ng/kg.bw/day) of PFAAs via consumption of wheat and maize separately for various age groups

Location	Objectives	The EDIs via consumption of wheat						The EDIs via consumption of maize					
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	∑PFAAs	PFBA	PFPeA	PFHxA	PFHpA	PFOA	∑PFAAs
CR	Toddlers	1219.24	256.39	141.47	10.11	44.93	1674.14	5.63	0.48	0.96	0.16	0.15	7.53
	Children	1228.09	258.25	142.50	10.19	45.25	1686.29	5.67	0.48	0.96	0.17	0.15	7.59
	Teenagers	934.12	196.43	108.39	7.75	34.42	1282.63	4.32	0.37	0.73	0.13	0.12	5.77
	Adults	828.78	174.28	96.16	6.87	30.54	1138.00	3.83	0.33	0.65	0.11	0.10	5.12
1km	Toddlers	887.91	177.16	55.61	13.08	72.18	1208.00	6.41	1.44	2.61	0.03	0.15	10.75
	Children	894.36	178.45	56.01	13.17	72.70	1216.77	6.45	1.45	2.63	0.03	0.15	10.82
	Teenagers	680.27	135.73	42.60	10.02	55.30	925.51	4.91	1.10	2.00	0.02	0.11	8.23
	Adults	603.56	120.43	37.80	8.89	49.06	821.14	4.35	0.98	1.77	0.02	0.10	7.30
2km	Toddlers	81.56	17.64	7.84	1.36	17.48	127.46	1.46	0.43	0.91	0.10	0.11	3.15
	Children	82.15	17.77	7.89	1.37	17.61	128.39	1.47	0.43	0.91	0.10	0.11	3.17
	Teenagers	62.49	13.51	6.00	1.04	13.39	97.66	1.12	0.33	0.69	0.08	0.08	2.41
	Adults	55.44	11.99	5.33	0.93	11.88	86.64	0.99	0.29	0.62	0.07	0.08	2.14
4km	Toddlers	61.14	16.55	6.08	0.85	7.53	95.19	1.18	0.26	0.53	0.04	0.10	2.42
	Children	61.59	16.67	6.12	0.86	7.58	95.88	1.19	0.26	0.53	0.04	0.10	2.44
	Teenagers	46.85	12.68	4.66	0.65	5.77	72.93	0.90	0.20	0.40	0.03	0.08	1.85
	Adults	41.56	11.25	4.13	0.58	5.12	64.71	0.80	0.18	0.36	0.03	0.07	1.64
7km	Toddlers	32.98	7.47	2.10	0.60	5.24	51.63	0.45	0.10	0.30	0.04	0.09	1.13
	Children	33.22	7.53	2.11	0.60	5.28	52.01	0.45	0.10	0.30	0.04	0.09	1.14
	Teenagers	25.27	5.73	1.61	0.46	4.02	39.56	0.34	0.08	0.23	0.03	0.07	0.87
	Adults	22.42	5.08	1.43	0.41	3.56	35.10	0.30	0.07	0.21	0.03	0.06	0.77

10km	Toddlers	15.79	3.72	1.60	0.56	5.07	29.15	0.22	0.09	0.20	0.04	0.09	0.79
	Children	15.90	3.74	1.61	0.57	5.11	29.36	0.22	0.09	0.20	0.04	0.09	0.80
	Teenagers	12.10	2.85	1.22	0.43	3.88	22.33	0.17	0.07	0.15	0.03	0.07	0.61
	Adults	10.73	2.53	1.09	0.38	3.45	19.82	0.15	0.06	0.13	0.03	0.06	0.54

Note: The estimated daily intake (EDI, ng/kg·bw/day) of PFAAs through the consumption of wheat and maize can be calculated based on averaging the intake dose by body weight. The details of the calculation and data sources are shown in Table S6. Considering that body weights and consumption rates vary by age, the EDIs were estimated for four age groups: toddlers (2-5 years), children (6-10 years), teenagers (11-17 years), and adults (≥18 years). As for the EDI calculation for residents with different radius from the FIP, the average concentrations of PFAAs in wheat and maize grain collected in that radius were used.

Table S17. The total estimated daily intake (EDI, ng/kg·bw/day) of PFAAs via consumption of wheat and maize for residents around the FIP.

Location	Objectives	PFBA	PFPeA	PFHxA	PFHpA	PFOA	∑PFAAs
CR	Toddlers	1225	257	142	10.3	45.1	1682
	Children	1234	259	143	10.4	45.4	1694
	Teenagers	938	197	1094	7.87	34.5	1288
	Adults	833	175	96.8	6.99	30.6	1143
1km	Toddlers	894	179	58.2	13.1	72.3	1219
	Children	901	180	58.6	13.2	72.8	1228
	Teenagers	685	137	44.6	10.0	55.4	934
	Adults	608	121	39.6	8.91	49.2	828
2km	Toddlers	83.0	18.1	8.74	1.47	17.6	131
	Children	83.6	18.2	8.81	1.48	17.7	132
	Teenagers	63.6	13.8	6.70	1.12	13.5	100
	Adults	56.4	12.3	5.94	1.00	12.0	88.8
4km	Toddlers	62.3	16.8	6.61	0.89	7.63	97.6
	Children	62.8	16.9	6.65	0.90	7.69	98.3
	Teenagers	47.7	12.9	5.06	0.68	5.85	74.8
	Adults	42.4	11.4	4.49	0.61	5.19	66.4
7km	Toddlers	33.4	7.58	2.40	0.64	5.33	52.8
	Children	33.7	7.63	2.42	0.65	5.37	53.2
	Teenagers	25.6	5.81	1.84	0.49	4.08	40.4
	Adults	22.7	5.15	1.63	0.44	3.62	35.9

10km	Toddlers	16.0	3.81	1.79	0.60	5.16	29.9
	Children	16.1	3.83	1.81	0.61	5.19	30.2
	Teenagers	12.3	2.92	1.37	0.46	3.95	22.9
	Adults	10.9	2.59	1.22	0.41	3.51	20.4

Note: toddlers (2-5 years), children (6-10 years), teenagers (11-17 years), and adults (⩾18 years).

Figures

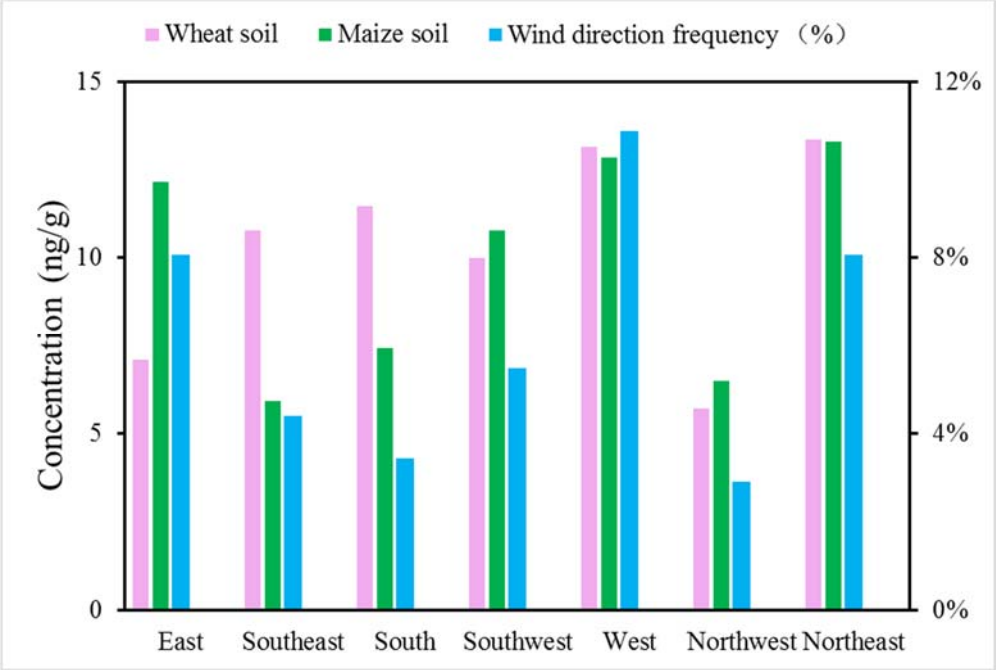

Fig S1. The concentrations of PFAAs in wheat and maize soil in different directions and their corresponding wind frequencies.

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